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THE
THEORY OF EMULSIONS AND THEIR TECHNICAL TREATMENT

BY

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PREFACE

SINCE the appearance of the preceding edition much valuable work has been reported on the general theory of emulsions. Outstanding have been the papers published from Cambridge by Dr. J. H. Schulman and his co-workers and from the Imperial College by Dr. A. King and several collaborators. Advances have been made in all aspects of the subject.

Evidence of the importance now given to emulsions and related problems is seen in the two General Discussions before the Faraday Society on the electrical double layer (Sept. 1939) and the oil/water interface (Jan. 1941) respectively. Very important also is the publication (in English) of the papers presented in 1937 to the colloid chemistry section of the Nederlandsche Chemische Vereeniging dealing with the electrical double layer. The British section of the International Society of Leather Trades' Chemists held a symposium in London in 1937, the papers with my Foreword being published later in a volume entitled : " Wetting and Detergency." Its relation to emulsions is obvious.

The patent literature has broadened widely and is now so extensive that only selected specifications can be mentioned. However, so many patents have been referred to that the present text should be of real guidance to Patent Agents.

All the above sources have been taken into account in preparing the present edition. The circumstances accompanying the revision have been far from propitious. Nevertheless, an attempt has been made to delete older matter and to bring out modern results and opinions. Rearrangement of the opening chapters has been necessary properly to introduce the newer investigations. The necessity to avoid unduly enlarging the text has resulted in furnishing numerous references where the written account has been abbreviated. It is felt that the literature has been covered in a thorough manner and the Author index lists nearly 2,000 references.

Industrial emulsions are now far too numerous to be treated adequately in a single volume. Rather must a selection be made of those emulsions which involve some special theoretical considerations and broad physico-chemical principles. This explains the inclusion of bitumen emulsions (problems of breaking), biological emulsions (problems of interfacial effects and inversion), insecticides and fungicides (problems of wetting), milk and butter (the influence of the air/liquid interface) and so forth.

My task has been lightened by the receipt of numerous reprints of papers which so many scientists have continued to send to me. I cordially thank them all and especially : Dr. D. H. Bangham (Egyptian University, Cairo) ; Dr. S. F. Barclay (Manchester) ; Dr. G. W. Boericke (Hahnemann Medical College, Philadelphia, Pa.) ; Dr. G. Broughton (Massachusetts Institute of Technology) ; Dr. A. S. Carpenter (Birmingham) ; Dr. H. M. Cassell (Palo Alto, California) ; Dr. F. A. Cooper (London) ; Mr. H. L. Davis (Westminster College, New Wilmington, Philadelphia, Pa.) ;

Dr. H. B. Dean (Cambridge); Dr. W. Ebeling (Riverside, California); the late Prof. H. Freundlich; Mons. M. R. M. Gattefossé (Lyon); Dr. C. W. Gibby (Durham); Dr. K. Gostkowski (Lwów, Poland); Dr. G. S. Hartley (London); Prof. E. A. Hauser (Massachusetts Institute of Technology); Dr. S. S. Joshi (Benares Hindu University); Dr. A. King (London); Dr. E. O. Kræmer (E.I. du Pont de Nemours & Co. Inc.); Dr. E. Lange (Erlangen); Mr. C. S. Lawrence (British Bitumen Emulsions, Ltd.); Prof. W. C. M. Lewis, F.R.S. (University of Liverpool); Dr. H. Martin (Long Ashton, Bristol); Prof. J. W. McBain, F.R.S. (Stanford University); Mr. L. T. Monson (Los Angeles, California); Dr. L. S. Moyer (University of Minnesota); Dr. S. Oka (Osaka Imperial University, Japan); Dr. J. B. Parke (Queen's University, Belfast); Dr. R. C. Pink (Queen's University, Belfast); Dr. H. Platenius (Cornell University, Ithaca, N.Y.); Dr. J. Powney (London); Mr. G. B. Shea (U.S. Bureau of Mines, San Fransisco); Dr. K. Söllner (Cornell University, Ithaca, N.Y.); Dr. C. H. Spiers (London); Prof. N. S. Stroganow (Moscow); Dr. C. G. Sumner (London); Prof. E. R. Theis (Lehigh University, Bethlehem, Pa.); Prof. S. Tomotika (Osaka Imperial University, Japan); Dr. P. A. Young (Bozeman, Montana).

It has been my happy lot to have had a team of young enthusiastic colleagues working on academic and technical aspects of the bulk production of emulsions. Since 1927 these men have carried out a very wide range of investigations from which I have learned much. In the main such work is not published. Recognition is, however, due and I now express my appreciation and gratitude to: Sydney Back, B.Sc., F.I.C.; George Reginald Barnes, M.Sc. Tech., A.I.C.; Mrs. G. R. Barnes (Gertrude Gell, B.Sc., A.I.C.); Vincent Anthony Cachia, B.Sc., A.I.C.; Otto Bernhard Darbishire, B.Sc., A.R.C.S., A.I.C.; Harry Kenneth Dean, B.Sc., Ph.D., A.I.C.; Alfred John Howard, M.A.; Robert Ian Johnson, B.Sc., A.I.C.; Robert Macdonald Kerry, B.Sc., A.I.C.; William George Mitchell; James Frederick Morse; Cyril Gordon Sumner, M.Sc., Ph.D., A.I.C.

Interest in emulsions has made me many friends and brought me into touch with a long list of scientists at home and abroad. There is real satisfaction in the call for a fourth edition during these troubled times.

Permission to reproduce tables and figures has been readily given by the Editors of the several scientific journals from which the new matter has been culled. My best thanks are extended to these authorities. For much patience and great care I am, as on previous occasions, in the debt of my Publishers.

WILLIAM CLAYTON

ORPINGTON, KENT.

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EMULSIONS

CHAPTER I

SURFACE PHENOMENA

An emulsion is a system containing two *liquid* phases, one of which is dispersed as globules in the other.[1] That liquid which is broken up into globules is termed the dispersed phase, whilst the liquid surrounding the globules is known as the continuous phase or dispersing medium. The two liquids, which must be immiscible or nearly so, are frequently referred to as the internal and external phases respectively.

For two given liquids O and W two sets of emulsions are theoretically possible, depending upon whether O is dispersed in W, or *vice versâ.* Also, there is no *à priori* reason why emulsions of any desired concentration should not be made of either liquid in the other.[2]

Two very distinct classes of emulsions exist: (*a*) dilute, simple emulsions of oil-in-water, (*b*) concentrated and more complex emulsions of oil-in-water or water-in-oil. The emulsions in the second class contain a third substance, the presence of which confers stability or permanence to the system. The simple dilute emulsions are important for their bearing on the general theoretical treatment of colloidal suspensions. The complex emulsions introduce considerations of surface and interfacial tension and the structure of interfaces, and they are the more important emulsions from the technical standpoint.

Although emulsions primarily concern phenomena arising from and at liquid/liquid interfaces, a rational treatment cannot ignore the extensive modern work dealing with the surfaces of liquids, the air/liquid interface, since many of the effects there observed apply, with or without modification, to the liquid/liquid interface. Surface tension and interfacial tension have much in common. Adsorption is effected at both kinds of interface, so that foam and emulsions admit of somewhat similar considerations.

SURFACE TENSION

Several well-known facts concerning the behaviour of liquids suggest that the free surface, the gas/liquid interface, acts as a kind of elastic envelope which endeavours to reduce the mass to minimum volume. This tension, of which the fundamental property is to decrease surface area, is termed the surface tension, and, important to note, its value is independent of the size of the liquid surface. Extension of a liquid surface isothermally requires work to be done (surface free energy), whence surface tension may be regarded as the free surface energy per unit of surface, expressed as ergs/cm.^{2} Numerically identical is the more usual expression of surface tension as dynes/cm., the force acting on unit length of the surface parallel to the surface and perpendicular to the unit length itself.[1]

---

[1] F. Selmi, *Nuovi Ann. d. Scienze Naturali di Bologna,* Serie II., t. IV., p. 146 (1845), quite clearly gives this definition of an emulsion; cf. Hatschek's "Foundations of Colloid Chemistry" (London, 1925), p. 32.

[2] An extension of this to alloys has been made by Gillet (*J. Phys. Chem.,* **20,** 729 (1916)); cf. also Bancroft (*Chem. Met. Eng.,* **26,** 391 (1922)).

Fundamentally involved in considering the origin of surface tension is the theory of molecular attraction in liquids and the problem whether a liquid maintains a uniform density up to its vapour phase or whether there is a gradual transition from liquid to vapour.[2]

The usual elementary view of surface tension, due to Laplace,[3] is based on the theory that the molecules in the surface of a liquid experience an inward pull of considerable magnitude due to the attraction of the molecules in the interior of the liquid. The molecules in the bulk of the liquid are attracted on all sides, whilst those at the surface are subjected to an unbalanced attraction. The peculiar condition of tension at the surface of a liquid is ascribed as being due to this inward pull on the surface molecules.

On this view the enlargement of a liquid surface requires work to be done against forces which operate at right angles to the surface. Frequently, the term *capillary layer* is accorded to the layer wherein the forces are unbalanced.

In contrast to the Laplacian theory which assumes that the density of the liquid is uniform with abrupt transition at the liquid/vapour boundary,[4] van der Waals proposed a theory based on the continuous transition of the density of a liquid to that of the vapour phase.

Shereshefsky[5] has pointed out that neither of these theories allows for the calculation of the thickness of the transitional layer except by the use of an arbitrary potential function. In his opinion, the capillary layer is constituted by the unimolecular transition layer of the liquid together with an adsorbed phase of the vapour (denser than the bulk vapour phase but less dense than the liquid). The adsorbed vapour in the capillary layer is due to the attraction exerted by the molecules in the liquid layer. This author calculates that the thickness of the adsorbed vapour layer does not exceed one molecule. Moreover, the thickness of the capillary layer is calculated to remain constant over the entire temperature range wherein the substance is in the liquid state. "A comparison of the densities in the three phases shows that, while the density of the condensed phase is from seven to ten times greater than the density of the vapour phase, the former is from sixty to two hundred times smaller than the density of the liquid." It is inferred, therefore, that the transition from the liquid to the adsorbed phase is abrupt.

---

[1] Detailed mathematical discussions are given by: Bouasse, "Capillarité: Phénomènes Superficiels" (Paris, 1924); Bakker, "Kapillarität und Oberflächenspannung" (Leipzig: 1928); Herčík, "Oberflächenspannung in der Biologie und Medizin" (Leipzig, 1934); Gatty and McKay, *Phil. Mag.*, **22,** 402 (1936); Lennard-Jones and Corner, *Trans. Faraday Soc.*, **36,** 1156 (1940); Gogate and Kothari, *Phil. Mag.*, **20,** 1136 (1935). See also Traube, *J. Chem Education*, **17,** 324 (1940) on "The Earliest History of Capillary Chemistry."

[2] For detailed accounts see Edser, *Brit. Assoc. Colloid Repts.*, **4,** 40 (1922); Taylor, "A New View of Surface Forces" (Toronto, 1925); Adam, "The Physics and Chemistry of Surfaces" (Oxford, 1930); Herčík, "Oberflächenspannung in der Biologie und Medizin" (Leipzig, 1934); Rabinowitsch, Bach and Passynski, "Theorie der Oberflächenerscheinungen" (Moscow, 1934).

[3] *Vide* Maxwell and Rayleigh, *Enc. Brit.*, "Capillarity"; Hatschek and Willows, "Surface Tension and Surface Energy" (London, 1915); Edser, "General Physics for Students" (1926), Chaps. IX. and X., and Appendix IV.; Hardy, *Nature*, **109,** 375 (1922); Brillouin, *J. Phys. Radium*, **9,** 462 (1938); Giacalone, *Gazz. chim. ital.*, **70,** 37 (1940).

[4] *Vide* Mokrushin, *J. Phys. Chem.*, **32,** 879 (1928).

[5] *J. Phys. Chem.*, **36,** 1271 (1932); cf. Williams, *Mem. Proc. Manchester Lit. Phil Soc.*, **68,** Part I (1924); Bowden and Bastow, *Nature*, **135,** 828 (1935). McBain, *J. Chem. Phys.*, **7,** 818 (1939), finds that the least possible thickness of the water surface is 2-3Å.

THE PARACHOR

It will be readily appreciated that the surface tension of a liquid will be related to other physical properties dominated by molecular constitution.[1]

An empirical equation to McLeod [2] related the density (D) of a liquid and its surface tension (σ). The relation is that $\frac{\sigma}{(D - d)^4} = C$ where d = vapour density and C = constant, depending on the liquid. Sugden [3] developed from this the value P, his so-called Parachor. If M = molecular weight of the liquid, $\frac{M\sigma^{\frac{1}{4}}}{D - d} = MC^{\frac{1}{4}} = P$. At temperatures low enough for d to be neglected, $P = \frac{M}{D}\sigma^{\frac{1}{4}}$ where $\frac{M}{D}$ = molecular volume. The calculation of the Parachor from the chemical composition of compounds has been effected with considerable accuracy and is a valuable tool in elucidating the structure or constitution of compounds.[4]

ADSORPTION

Before discussing other aspects of surface tension, particularly modern developments, it is necessary to present briefly the principles underlying concentration changes at the air/liquid interface, these being closely connected with the observed time effects.

It can be shown on thermodynamical grounds that, if a third substance now be added which will affect the value of the surface tension, concentration phenomena appear, *i.e.*, the concentration of the added substance will be different in the main bulk of the continuous phase from what it is at the interfacial separating surface. The most stable arrangement accompanying interfaces in general is that the surface energy should be a minimum. Consequently, if a dissolved substance raises the potential energy at the interface, it will tend to leave that interface ; if it diminishes the potential energy, then it will concentrate at the interface. This is in accordance with the Le Chatelier-Braun principle of "mobile equilibrium."

---

[1] Conrad and Hall, *J. Am. Chem. Soc.*, **57**, 863 (1935) ; Lautie, *Bull. soc. chim.*, **2**, 155 (1935) ; Uhlig, *J. Phys. Chem.*, **41**, 1215 (1937) ; Buehler, *ibid.*,, **42**, 1207 (1938) ; Irany, *J. Am. Chem. Soc.*, **61**, 1436 (1939) ; Bolton and Evans, *Trans. Faraday Soc.*, **37**, 1 (1941).

[2] *Trans. Faraday Soc.*, **19**, 38 (1923).

[3] *J. Chem. Soc.*, **125**, 1177 (1924). For a critical review see Bayliss, *Australian Chem. Ihst., J. and Proc.*, **2**, 81 (1935).

[4] Recent developments are reflected in the following papers : Aten, *Rec. trav. chim.*, **54**, 666 (1935) ; Manzoni-Ansidei, *Giorn. biol. ind., agrar. aliment.*, **7**, Nos. 3 and 5 (1937) ; Corriez, *J. pharm. chim.*, **26**, 299 (1937) ; Fowler, *Proc. Roy. Soc.*, A **159**, 229 (1937) ; Larson and Hunt, *J. Phys. Chem.*, **43**, 417 (1939) ; Rădulescū, *Kolloid-Z.*, **87**, 280 (1939) ; Rougeot, *Bull. soc. chim.*, **6**, 794 (1939) ; Bogdan, *Compt. rend.*, **208**, 2069 (1939) and *Bull. sect. sci. acad. roumaine*, **22**, 104 (1939) ; Lewis, *Nature*, **145**, 551 (1940).

Concentration changes at an interface are termed *adsorption*. Classical treatment of the problem in thermodynamics was given by Willard Gibbs,[1] who deduced a "fundamental equation for the surface of discontinuity."

THE GIBBS THEOREM

Donnan[2] has presented a simple account of the basic features of Gibbs' monumental work in these words: "The fundamental idea underlying Gibbs' method of investigation was the introduction of terms denoting the *superficial densities* of energy, entropy and of the several component substances. He defined this superficial density as the *excess*, per unit of interfacial area, of the quantity in question in the interfacial film over and above the amount which would have been present if the homogeneous masses had extended without alteration of any sort right up to the dividing surface. In this way he obtained for the equilibrium state fundamental equations relating to the interface, as, for example:

$$u_s = ts_s + \sigma + \mu_1\Gamma_1 + \mu_2\Gamma_2 + \text{etc.}$$
$$d\sigma = -s_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \text{etc.}$$

where u_s and s_s denote the interfacial excess amounts (superficial densities) of energy and entropy, respectively, Γ_1, Γ_2, etc., the interfacial excess amounts of the several components, μ_1, μ_2, etc., the potentials of the components in the homogeneous masses in equilibrium and σ a quantity which will generally be sensibly equal to the interfacial tension as experimentally measured."

Gibbs considered a very thin non-homogeneous film, constituting a surface of discontinuity, separating two fluid masses. It is imagined that each of the homogeneous masses extends up to the dividing surface unchanged as regards the densities of its several components or as regards the densities of energy and entropy. This dividing surface is considered sensibly coincident with the physical surface of discontinuity.

Thus, σ is regarded as a function of t, μ_1, μ_2, etc., from which, if known, Γ_1, Γ_2, may be determined in terms of the same variables.

Gibbs, in considering the case of liquid mercury meeting the mixed vapours of water and mercury in a plane surface, arbitrarily places the dividing surface so that the surface concentration Γ_1 is zero. If Γ_2 denotes the *adsorbed* water on the mercury surface (representing "the amount of water in the vicinity of the surface above that which there would be if the water vapour just reached the surface without change of density "), then :

---

[1] "Scientific Papers," Vol. I. (1906), p. 219 *seq.* See also: Guggenheim, "Modern Thermodynamics by the Methods of Willard Gibbs" (London, 1933), p. 160. The Gibbs potential is defined by Brønsted, *Kgl. Videnskab. Selskab. Math.-fys. Medd.*, **12,** No. 6, 7 pp. (1933). An elementary deduction of Gibbs' adsorption theory is given by Guggenheim, *J. Chem. Physics*, **4,** 689 (1936). Van Rysselberghe, *J. Phys. Chem.*, **42,** 1021 (1938) deals with "Conventions and Assumptions in the Interpretation of Experimental Data by Means of the Gibbs Adsorption Theorem." See also Döring and Neumann, *Z. physik. Chem.*, **A., 186,** 193 (1940).

[2] "The Influence of J. Willard Gibbs on the Science of Physical Chemistry." The Franklin Institute, Philadelphia (Sept., 1924), p. 21.

$$\Gamma_2 = -\frac{d\sigma}{d\mu_2}$$

at constant temperature. Assuming the pressures in the mixed vapours to obey Dalton's law, at constant temperature :

$$dp_2 = cd\mu_2$$

Here p_2 = the part of the pressure in the vapour contributed by the water vapour, whose density is c. Then :

$$\Gamma_2 = -c\frac{d\sigma}{dp_2}.$$

From the relation, $P = RTc$, the gas law, there obtains,

$$\Gamma_2 = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}.$$

Various derivations[1] of this famous equation have been given either by the analytical method or by a cyclic process.

Since $\frac{d\sigma}{dc}$ is the differential coefficient of the function connecting *surface* or *interfacial* tension and concentration, it follows that $\frac{d\sigma}{dc}$ is positive when the solute increases the tension, and negative when it decreases it. Consequently, Γ is positive when the added substance lowers the tension, *i.e.*, the added substance will be adsorbed at an interface if by its adsorption the boundary tension is reduced.

The surface excess per unit of area (Γ), at the surface of a solution was originally defined as the difference between the quantity of solute contained in a given volume of solution containing unit area of free surface and that in an equal volume without any free surface. The dependence of the values of Γ on the exact position assigned to the hypothetical geometrical surface has been discussed in detail by Guggenheim and Adam.[2] The Gibbs equation has also been generalised to hold for interphases of finite thickness and small radius of curvature.[3]

Oka[4] has combined the thermodynamic equation with the Debye-Hückel theory. In the case of dilute electrolyte solutions, he calculates the thickness of the capillary layer as 10–20 Å. Herzfeld,[5] also dealing with not too concentrated solutions, found that for a range of molecular attraction of the order of 10^{-7} cm., the maximum increase in σ at room temperature is 2·5 ergs/cm.^{2} for 1 mol./litre.

---

[1] Thomson, "Applications of Dynamics to Physics and Chemistry" (1888), p. 190; Milner, *Phil. Mag.*, **13**, 96 (1907); Harlow and Willows, *Trans. Faraday Soc.*, **11**, 53 (1915); Porter, *ibid.*, **11**, 51 (1915); Harkins, *J. Am. Chem. Soc.*, **39**, 551 (1917); Lunn, *ibid.*, **41**, 986 (1919); Iredale, *Phil. Mag.*, **48**, 1088 (1923); Volmer, *Z. physik. Chem.*, **115**, 253 (1925); Pavlov, *Kolloid-Z.*, **35**, 89 (1924); Koenig and Swain, *J. Chem. Physics*, **1**, 723 (1933); Defay, *Bull. sci. acad. roy. Belg.*, (v), **15**, 849 (1929); Morton, quoted by Lewis, *Phil. Mag.* (April, 1908), p. 504.

[2] *Proc. Roy. Soc.*, **A.**, **139**, 218 (1933). See also Schofield and Rideal, *Phil. Mag.*, **13**, 806 (1932); van Rysselberghe, *J. Phys. Chem.*, **42**, 1022 (1938); Guggenheim, *Trans. Faraday Soc.*, **36**, 397 (1940).

[3] Craxford, Gatty and Philpot, *Phil. Mag.*, **17**, 54 (1934).

[4] *Proc. Phys.-Math. Soc. Japan*, **14**, 649 (1932).

[5] *Z. physik. Chem.*, **107**, 74 (1923).

THE ADSORPTION ISOTHERM

Besides the Gibbs equation it is necessary to mention the widely-used adsorption isotherm, associated more particularly with the name of Freundlich.[1] This is a purely empirical relation, frequently, though erroneously, referred to as the adsorption exponential equation. If

m = mass of adsorbing material in grams,
x = amount of solute adsorbed by this mass,
C = the final or equilibrium concentration of the solute,

then
$$\frac{x}{m} = aC^{\frac{1}{n}}$$

where a and n are constants ($n > 1$) for a given solute and adsorbing material (adsorbent). Since the exponent $\frac{1}{n}$ is a constant, the equation is that of a general parabola. For representing experimental results on adsorption it is usual to express the equation in a logarithmic form, viz.,

$$\log x - \log m = \frac{\log C}{n} + \log a.$$

This is the equation of a straight line; the graph obtained by plotting log x against log C, the two variables, is a straight line.

One important fact is immediately evident from inspection of the adsorption isotherm, or " concentration function " as it is now frequently termed, viz., the extent of adsorption is relatively more pronounced in dilute solution, the amount adsorbed increasing with, but more slowly than, the concentration. Adsorption at interfaces, whether air/liquid or liquid/liquid, takes place very rapidly, and in certain instances the resulting adsorbed film becomes saturated at surprisingly low concentrations of the solute.

Other formulæ have been given by various investigators, and certain peculiarities and anomalies in connection with adsorption pointed out.[2] The adsorption isotherm will concern us only in so far as it has been applied in investigations on emulsions.

RECENT THEORIES OF SURFACE TENSION

Onsager and Samaras,[3] expand a theory by Wagner,[4] based on the Gibbs theorem and on the unbalanced distribution of ions between the interior and the surface of the liquid, calculated from the difference of potential energy between an ion at the surface and one in the interior. The Debye-Hückel conception of ionic atmospheres and image charges at the air/liquid boundary is invoked.

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[1] " Kapillarchemie " (1909), p. 147; cf. Swan and Urquart, " Adsorption Equations—A Review of the Literature," *J. Chem. Phys.*, **31,** 251 (1927). Donnan, *loc. cit.*, p. 25, gives the derivation of the Freundlich from the Gibbs equation. See also Cremer and Flügge, *Z. physik. Chem.*, B. **41,** 453 (1938).

[2] Cunningham, *J. Phys. Chem.*, **39,** 69 (1935); Boutaric, *J. chim. phys.*, **26,** 492 (1929); **35,** 158 (1938); Bennett, *J. Chem. Education*, **9,** 517 (1932); Tamamushi, *Bull. Chem. Soc. Japan*, **8,** 120 (1933); *Kolloid-Z.*, **71,** 150 (1935); Bancroft, *J. Phys. Chem.*, **31,** 1501 (1927); Cernuschi, *Proc. Cambridge Phil. Soc.*, **34,** 392 (1938); Wang, *ibid.*, **34,** 238 and 412 (1938); Zel'Dovich, *Acta Physicochim.* (*U.S.S.R.*) **1,** 961 (1934) in English.

[3] *J. Chem. Physics*, **2,** 528 (1934).

[4] *Physik. Z.*, **25,** 474 (1924).

Jones and Ray[1] have pointed out that Onsager and Samaras considered only the electric forces between the ions, neglecting the electric forces between the ions and the water molecules considered as electric dipoles. Yet the electric forces between the dipolar water molecules must tend to maintain a systematic or ordered arrangement. "If we add a salt to water in such great dilution that the interionic forces are negligible, there must nevertheless be a disturbance of the normal arrangement of the water molecules in the vicinity of the ions. The electric forces between the water dipoles would oppose this disturbance and tend to thrust the disturbing ions out into the surface, thus causing positive adsorption. In view of the electrically unsymmetrical character of the water molecules, this force may well be different for positive and negative ions. Since the cohesion, and therefore also the surface tension, of water is probably largely due to the electric forces between the dipoles, a disturbance of the normal electric distribution may cause a diminution of the surface tension. As the solution becomes more concentrated (about 0·01 N or above), the mutual attraction between ions of opposite polarity becomes stronger than the forces between the ions and the water molecules and causes negative adsorption and an increase in surface tension in the manner discussed by Onsagar and Samaras. We may conclude, therefore, that the treatment of Onsagar and Samaras is over simplified and thus fails to give a complete and accurate result."

Recently, Jones and Ray[2] have extended their investigations on the surface tension of solutions of electrolytes as a function of the concentration. Their aim was to settle whether or not it is a general rule that salts which are capillary-inactive at moderate concentrations exhibit a minimum in their σ/concentration curves, indicating at sufficiently low concentrations capillary activity. Eight salts were chosen: $LaCl_2$; $BaCl_2$; $KClO_3$; KSCN; LiF; CsI; $K_3Fe(CN)_6$; $K_4Fe(CN)_6$.

Just as previously with KCl, K_2SO_4 and $CsNO_3$, these eight salts agree in that the first addition of salt causes a decrease in surface tension and there is a minimum in the σ/concentration curve at a low concentration of the order of 0·001 N. "Since all eleven salts which have been studied show this behaviour without exception and since the salts were purposely chosen to differ greatly among themselves in valence-type, in size of the ions, in degree of hydration, and in complexity, the probability that this is a general characteristic property of salts is enormously increased by our new data. . . . At all concentrations above the minimum, the slope of the σ/concentration curves is positive, which means that the surface layer is depleted of salt. This negative adsorption is at least qualitatively in accord with predictions based on the Debye theory of interionic attraction. At the minimum in the curve, there is neither positive nor negative adsorption, which means that there is a balance between the forces causing positive adsorption at extreme dilution, and the interionic forces which draw the ions away from the surface. These opposing forces are evidently very different functions of the concentration. The former are dominant at extreme dilution (under about 0·001 N) and the latter become more effective at higher concentrations."

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[1] *J. Am. Chem. Soc.*, **59**, 187 (1937).

[2] *Ibid.*, **63**, 288 (1941).

Following the first paper by Jones and Ray, Dole [1] proposed a theory of surface tension of aqueous solutions which would be in accord with the so-called *Jones effect*, *i.e.*, the initial decrease of surface tension with concentration, followed by a minimum and then an increase. The main idea underlying Dole's treatment is that the forces in the first adsorption layer are much more important for the understanding of the Jones effect than the weaker, relatively long range mirror-image forces discussed by Onsager and Samaras.

Not only must the fact of adsorption of ions at the interface be explained but there must be elucidated the mechanism by which this positive adsorption terminates at a low concentration and be replaced by negative adsorption. Ion-dipole interactions must be involved and the mechanism must depend largely on the properties of the solvent. The special property assumed by Dole is the existence of a special orientation or grouping of water molecules in a limited number of locations or "active spots" on the water surface, and in such configuration that *negative* ions will be attracted to these spots from the interior of the solution, *i.e.*, a configuration with the proton ends of several contiguous surface water molecules pointing inward. There is no necessary assumption for the active spots to be fixed in position ; they may appear from time to time at different points in the surface. About four active spots are postulated for every 100,000 water molecules.

On this hypothesis negative ions will be adsorbed at the surface until all the active spots in average time are occupied, and then the σ/concentration curve will pass through a minimum. At higher concentrations no more negative ions can become adsorbed ; they will be repelled from other places in the surface layer by virtue of the mirror-image forces (Wagner, Onsager and Samaras) or by other repulsive forces existing in the first adsorption layer (Langmuir).

From such arguments Dole derived a general equation for the variation of surface tension with change of concentration, which includes an empirical constant for the number of surface adsorbing spots per sq. cm. This equation was tested with the data of Jones and Ray and found valid.

From a rapidly growing literature in this new conception of surface tension the student is recommended to read the papers by Belton [2] and Pappenheimer, Lepie and Wyman.[3] The former summarises his thesis by stating that the extent of the salting out of non-electrolyte molecules in films adsorbed at the surface of solutions of electrolytes can be related to the polarisability and the permanent moment of the non-electrolyte, the charge on the ions and the dielectric constant of the medium. The other workers investigated the surface tension of aqueous solutions of seven amino acids of differing size and moment and of glycine betaine. Four amino acids increased the surface tension of water and the others decreased it. Thus in these dipolar ions there appears to be an antagonism between the effect of the electric moment (tending to increase the surface tension) and the size and number of organic groups in the molecule (which tend to decrease it).

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[1] *J. Am. Chem. Soc.*, **60**, 904 (1938).
[2] *Trans. Faraday Soc.*, **33**, 1449 (1937).
[3] *J. Am. Chem. Soc.*, **58**, 1851 (1936).

Dealing with reversible adsorption in the surface of soap solutions, McBain and Wilson [1] pointed out that many substances greatly depress the surface tension of water in dilute solution but the surface tension then passes through a minimum and rises again with increasing concentration. Yet the Gibbs equation predicts marked adsorption in the free surface of the dilute solutions, followed by no adsorption at the minimum where the slope is horizontal, followed by negative adsorption for all the higher concentrations. Paradoxically, "where the surface tension is most greatly lowered there is no adsorption to cause the lowering, and where the surface tension is still low the surface-active material is supposed to be relatively absent from the surface." Experiments with aqueous solutions of potassium laurate showed that the adsorption in the surface is reversible and that many hours must pass for adsorption to be complete.

McBain [2] introduced the conception of *pre-Gibbs adsorption* by surface re-arrangement. The suggestion is that lowering of the surface tension is due not solely to orientation of solute molecules by chance originally exposed on the surface, but also to an interchange of positions between molecules of solute and solvent within a few molecular diameters of the surface. Thus, a solution might almost immediately be partially covered by a layer of solute exposing only hydrocarbon groups and overlying another layer that would be mainly water. Complete coverage could lower the surface tension by more than 30 dynes/cm. This would explain the inability of oleic acid to spread on the surface of a soap solution, yet spreading immediately upon water and most aqueous solutions.

When a 0·15 per cent. solution of hydrocinnamic acid, whose surface tension is almost instantaneously depressed by at least 10 dynes/cm., is examined by the microtome method it appears that the Gibbs adsorption is negligible, the average composition of the surface sandwich layers being still that of the whole solution. The Gibbs adsorption takes twelve hours to rise to its approximate complete value.

The pre-Gibbs adsorption and the relatively slow solubility of the Gibbs layer can explain the fact that a moving bubble may yield reproducible values for adsorption which may range from many times smaller to many times larger than the Gibbs adsorption.

THE PLAWM TROUGH

McBain's school has advanced the experimental technique for the direct measurement of the absolute amount of adsorption in liquid surfaces.[3]

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[1] *J. Am. Chem. Soc.*, **58**, 379 (1936).

[2] *Nature*, **137**, 659 (1936).

[3] **Ford and McBain, *J. Am. Chem Soc.*, 58, 378 (1936) ; McBain and Swain, *Proc. Roy.***

Notably, there is the so-called PLAWM trough (Pockels-Langmuir-Adam-Wilson-McBain trough).[1] This consists of a film balance divided into two compartments by a water-tight flexible, rubber float, thus contrasting with the earlier superficial floating barrier.[2] This apparatus enables measurement of surface tension under the essential conditions that the surface is swept free from contamination, is static and undisturbed, and is free from evaporation during an adequate period for observation.

From results reached with the PLAWM trough three typical curves are noted when surface tension (ordinates) is plotted against concentration (abscissæ) :—

Type I. : the surface tension continually falls as concentration increases, first quickly and then more gradually. This case corresponds to the requirements of the Gibbs theorem that positive adsorption of the solute must occur.

Type II : the surface tension at once quickly rises above the value for water. Adsorption is negative, whereby it follows that in the surface layer there must be either a decreased concentration of solute or an excess of solvent.

Type III. : this is the most interesting type of curve. The surface tension at first falls steeply in very dilute solutions, passes through a minimum and then with increasing concentration rises although always below the value for water.

Lauryl sulphonic acid critically established [3] the existence of Type III. curves of surface tension with a minimum in extremely dilute solutions.

Type III. curves [4] are particularly significant since the positive adsorption actually observed by various methods does not accord with the requirements of the Gibbs theorem as usually applied to surface tension data. Even in non-ionising media the Type III. curve may be shown, *e.g.*, lauryl sulphonic acid dissolved in Nujol, mineral oil and hydrogenated tetraisobutylene.[5]

McBain's explanation of the minimum exhibited in a Type III. curve is based upon the submerged electrical double layer ; in increasing concentration the dissociation of electrolyte will diminish and permit the surface tension to rise. In non-ionising solvents a condensed Helmholtz double layer of the classical type is postulated in place of the partly diffusing type existing in water.

A detailed discussion of the anomalies in applying the Gibbs adsorption theorem to surface tension curves that exhibit minima in dilute solution has been presented by McBain and Mills.[6] This close examination deserves

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Soc., **A.**, **154**, 608 (1936) ; McBain, Ford and Wilson, *Kolloid-Z.*, **78**, I. (1937) ; Ford and Wilson, *J. Phys. Chem.*, **42**, 1051 (1938).

[1] McBain, Ford and Wilson, *Kolloid-Z.*, **78**, I (1937) ; McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939) ; McBain and Spencer, *J. Am. Chem. Soc.*, **62**, 239 (1940) ; McBain, Vinograd and Vincent, *ibid.*, **62**, 244 (1940) ; McBain and Sharp, *ibid.*, **63**, 1422 (1941).

[2] See Bakker, *Z. physik. Chem.*, **A.**, **171**, 49 (1934).

[3] McBain and Wood, *Proc. Roy. Soc.*, **A.**, **174**, 286 (1940) ; McBain, Vinograd and Wilson, *loc. cit.*

[4] McBain and Perry, *J. Am. Chem. Soc.*, **62**, 989 (1940).

[5] Previous illustrations of all three types of curves have been presented by Stroganow, *Protoplasma*, **24**, 439 (1935), with data on aqueous sugar/organic liquids boundaries.

[6] *Reports on Progress in Physics*, **5**, 30 (1939).

careful reading, noting, however, the contrary conclusions of Long and Nutting.[1]

McBain and Mills conclude that: "It follows from the Gibbs equation that the surface of solutions of soluble substances is very deep as compared with molecular dimensions, in contrast to the familiar conception of insoluble films on water. This is to some extent substantiated by the long time required to obtain equilibrium surface tensions for solutions and is also in accord with the novel phenomena recently discovered by applying the film balance and by measuring she rate of spread of oleic acid on solutions. The classical Gibbs adsorption theorem appears to be a limiting law applying to cases where mutual repulsion or oriented dipoles upon the surface and the effects of submerged double layer and of electrification do not also condition the surface tension."

Against this Long and Nutting argue: "It is well known that free electrical charges, introduced by *external means*,[2] do necessitate a different treatment. However, the great generality of the thermodynamic derivation of the Gibbs equation makes it apparent that all these phenomena, if of spontaneous origin, are within the scope of the equation."

Alexander,[3] following the tentative discussion by Powney and Addison,[4] has advanced a simple explanation of these anomalies, starting with acceptance of the idea that in the solutions thus treated micelle formation is initiated at concentrations close to and less than that at the minimum surface tension. It is further accepted that the micelle, due to its structure, cannot exist in the surface layer, wherein the single ionised molecule constitutes the surface active species. The activity term in the Gibbs equation, therefore, should be that for the *molecularly dispersed* solute in bulk solution. There is a "buffer" effect provided by the much larger amount of solute as micelles whereby the concentration of the molecularly dispersed solute remains sensibly constant. "Accordingly, it is not surprising that, using the activity of the solution *as a whole*, as McBain and Mills have done, the Gibbs equation should break down."

Alexander has calculated that the adsorption of lauryl sulphonic acid at the minimum surface tension (assuming the adsorbed film to be monomolecular) is + 5·7, in good agreement with that obtained by McBain and Wood[5] with the microtome technique, namely + 5·4 (gm. mol./cm.^{2} × 10^{10}).

The recent critical examination by Alexander[6] under the title: "The Structure of the Surfaces of Solutions" aims at showing that his previous results, taken in conjunction with well-established phenomena from the study of insoluble monolayers, provide a simple and detailed explanation of all the results of McBain and co-workers in this field. In all cases the adsorbed layer appears to be monomolecular in thickness.

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[1] *J. Am. Chem. Soc.*, **63**, 625 (1941).

[2] Du Bois and Todd, *ibid.*, **60**, 2355 (1938).

[3] *Nature*, **148**, 752 (1941).

[4] *Trans. Faraday Soc.*, **33**, 1252 (1937).

[5] *Proc. Roy. Soc.*, **A.**, **174**, 286 (1940).

[6] *Trans. Faraday Soc.*, **38**, 54 (1942).

Alexander first reviews the evidence for the adsorbed film being monomolecular in *dilute* solutions of hydrocinnamic and lauryl sulphonic acids. Listing five sets of data he concludes that the adsorbed film is monomolecular in thickness and that the " surface pellicle " has no real existence upon the static surfaces of the solutions.

Now follows an examination of the effect of compressing such an adsorbed monolayer, indicating that the orientated solute molecules may be unable to dissolve sufficiently rapidly and, therefore, may form micro-crystals on the surface, to redissolve comparatively slowly. The effects observed by McBain's school on ageing and compressing the surfaces of solutions, and the spreading of oils upon such solutions, are capable of ready interpretation from these ideas.

INTERPOLATION OF SURFACE TENSION

Various authors[1] have suggested methods to interpolate and extend surface tension data for different normal or unassociated organic liquids. Ferguson's equation is :—

$$\sigma = \mathrm{K}(\mathrm{T}_c - t)^n$$

where σ = surface tension,
T_c = the critical temperature,
K = a constant for the liquid under investigation,
n = 1·2 in the case of normal organic liquids.

Carr and Wolczynski[2] have shown that plotting the temperature at points of equal surface tension for a standard liquid and an unknown liquid gives a straight line. Accordingly, it is only necessary to know the surface tension of a standard liquid (such as chlorobenzene) over a fairly wide temperature range and two temperatures where the two liquids possess equal surface tensions, since at the critical temperature the surface tension for all liquids is zero.

The equation employed is $\frac{T_2 - \mathrm{T}_1}{\Theta_2 - \Theta_1} = \mathrm{K}$, where T_2 and T_1 are the temperatures of the unknown liquid where the surface tension values are the same as the values for the standard liquid at temparatures Θ_2 and Θ_1 respectively. K is the slope of the graph.

Provided the critical temperatures Θ_c and T_c of the liquids are substituted for Θ_2 and T_2 respectively, it is required to know only one other pair of temperatures in order to determine K. When K is determined, the line can be drawn when interpolation for surface tension is possible at all temperatures in this range. The authors' method is : " Through any temperature draw a line parallel to the horizontal axis and intersecting the line drawn through points of equal surface tension. Through this point of intersection draw a line parallel to the vertical axis and read the temperature of the reference substance under the same surface tension as that of the liquid in question. From the table for the standard liquid read the surface tension corresponding to this temperature. This will be the surface tension of the unknown liquid at the temperature originally chosen."

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[1] Van der Waals, *Z. physik. Chem.*, **13,** 716 (1894) ; Ferguson, *Science Progress*, **9,** 445 (1915) ; Sugden, *J. Chem. Soc.*, **125,** 32 (1924).

[2] *J. Am. Chem. Soc.*, **56,** 2541 (1934). See Morino, *Sci. Papers, Inst. Phys. Chem. Research* (Tokyo), **476,** 1–117 (1933) ; Ganguli and Mitra, *Current Sci.*, **4,** 23 (1935) ; Wheeler, *ibid.*, **3,** 550 (1935) ; Sibaiya, *ibid.*, **3,** 418 (1935) ; Boutaric, *J. chim. phys.*, **31,** 621 (1934) ; Hershey, *Phys. Rev.*, **56,** 204 (1939) ; Canals and Flous, *J. Pharm. Chim.*, **20,** 241 (1934) ; Tonomura and Ishihara, *Bull. Chem. Soc. Japan*, **9,** 439 (1934) ; Guareschi, *Atti accad. sci. Torino, Classe sci. fis. mat. nat.*, **74,** 137 (1939).

VARIATION OF SURFACE TENSION WITH TIME

The surface tension of fresh solution is frequently greater than that of the aged solution. Dupré[1] in 1869, and Rayleigh[2] in 1890, independently observed this phenomenon with soap solutions. The latter also noted the phenomenon with saponin solutions and expressed the view that the reduced surface tension was due to the presence of an insoluble film or pellicle of the solute on the surface of the aqueous solution. Milner's results[3] with aqueous sodium oleate confirmed the initial rapid fall in surface tension, followed by a gradual fall to a constant value. He believed that the soap was adsorbed in the surface until a definite concentration was acquired.

Other workers, including notably Lecomte du Noüy,[4] have studied the phenomenon in greater detail. Bigelow and Washburn[5] carried out very careful work by the method of capillary rise and the decrease with time of the surface tension of aqueous solutions of the following materials was noted: sodium oleate, sodium glycocholate, glycerol, phenol, resorcinol, pyrogallol, propionic acid, valeric acid and succinic acid. As example, whilst the fall of surface tension from an initial value (dynes/cm.) of 71·0 to 61·0 occurred in five minutes, the surface tension after 570 minutes was 42·4, the aqueous solution being M/4000 sodium oleate. Experimental evidence supported the theory that the organic solute was adsorbed at the glass/solution interface and at the solution/vapour interface.

Unexpectedly, they observed an *increase* with time in the case of aqueous solutions of amyl acetate, ethyl alcohol (2 per cent.), amyl alcohol, propyl alcohol, iso-propyl alcohol, ethylene dichloride and acetone. "With these solutions, after a rise to a maximum, the fresh surface formed by agitation displays the original minimum value from which another rise will start at once." The explanation advanced for this increase is that the solute evaporates from the surface of the solution more rapidly than replacement can be effected by diffusion from the bulk of the solution. Quantitative work with ethyl acetate and, later[1] with *n*-butyl acetate, agreed well with this hypothesis. Trimble[2] has also carried out similar investigations, using mixtures of organic liquids, as ether/acetone, ether/toluene, acetone/toluene, ether/CCl_4, and agrees that the changes with time of the surface tension of a mixture of liquids arises from the preferential evaporation of the more volatile liquid.

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[1] *Ann. chim. phys.*, **7,** 409 (1866); **9,** 379 (1866).

[2] *Proc. Roy. Soc.*, **47,** 281 (1890).

[3] *Phil. Mag.* (vi.), **13,** 96 (1907).

[4] "Surface Equilibria of Biological and Organic Colloids," (New York, 1926), Chap. 2. From experiments with aqueous solutions of benzopurpurin and brilliant green, Doss and Rao, *Proc. Indian Acad. Sci.*, **4A.,** II (1936), conclude that the ring method is unsuitable for ageing solutions.

[5] *J. Phys. Chem.*, **32** 321 (1928). Equations have been derived for the change with time of σ for solutions assuming that the delay in reaching equilibrium is due to the time required for the solute to reach the surface: Bond and Puls, *Phil. Mag.*, **24,** 864 (1937); Boutaric and Berthier, *J. chim. phys.*, **36,** I (1939).

Renewed interest in surface tension of solutions as a function of time is noted in several important investigations. Nutting, Long and Harkins[3] followed the change with time of the surface tension of aqueous solutions of sodium cetyl sulphate and sodium lauryl sulphate, the time effect extending over the interval between two minutes and about six hours over a wide range of concentrations and at particular concentrations in the presence of various inorganic salts. The effects noted are attributed mainly to the influence of the potential barrier set up against alkyl sulphate ions diffusing into the surface by the ions already in the surface film. The height of the barrier increases with the density of ions in the surface and initially is zero.

Later, Nutting and Long[4] investigated solutions of sodium laurate. Additional to the potential barrier effect they predicted a second retarding factor in the time required for stable orientation of the long, highly unsymmetrical ions in the surface film and the accompanying diffuse double layer. Hence, "a significant time effect may be expected among solutions of sodium salts of higher fatty acids (the soaps), with added complexities arising from the influence of hydrolysis on the surface active species."

Working with concentrations of soap solution from 0·001 N to 0·07 N and of *p*H from 7 to 11, they found that at *p*H 11 and concentrations less than the critical concentrations for micelle formation, the surface tension fell over a period of hours, the equilibrium value being a function of concentration. In micellar solutions the time effect was almost absent. With decreasing *p*H values the equilibrium surface tension and the time necessay to reach this diminish markedly, probably due to the possibility of closer packing of fatty acid molecules than ions in the surface film and the more rapid diffusion of non-ionised molecules into the surface region.

Alexander[5] has reviewed previous work on the surface ageing of solutions and favours the view that the experimental facts fit in with the idea of penetration and re-orientation at the surface, coupled perhaps with some dehydration of the hydrophobic portion. In aqueous solutions of ionised compounds such as the paraffin-chain salts there is probably a small electrical effect additionally.

For fuller reference to this phenomenon, Alexander's paper should be consulted, his examination of the theoretical aspect being unusually complete. Important to note are his findings that whilst at the air/water interface very many amphipathic compounds gave a very slow adsorption, at the oil/water interface this slow adsorption seemed to be invariably completely eliminated. This confirmed his earlier work with long-chain sulphates at the benzene-water interface and that of Powney and Addison using the xylene/water interface.

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[1] Washburn and Shildneck, *J. Am. Chem. Soc.*, **55**, 2354 (1933).
[2] *J. Phys. Chem.*, **32**, 1211 (1928).
[3] *J. Am. Chem. Soc.*, **62**, 1496 (1940).
[4] *Ibid.*, **63**, 84 (1941).
[5] *Trans. Faraday Soc.*, **37**, 15 (1941).

AGEING OF EGG ALBUMIN SOLUTIONS

Proteins present a special case regarding the σ/time curve. Change in the condition of the protein film at the air/liquid boundary of aqueous solutions complicates the matter and *p*H effect is profound. This surface change, *denaturation*, is particularly prominent in the foam produced by shaking protein solutions (see p. 28).

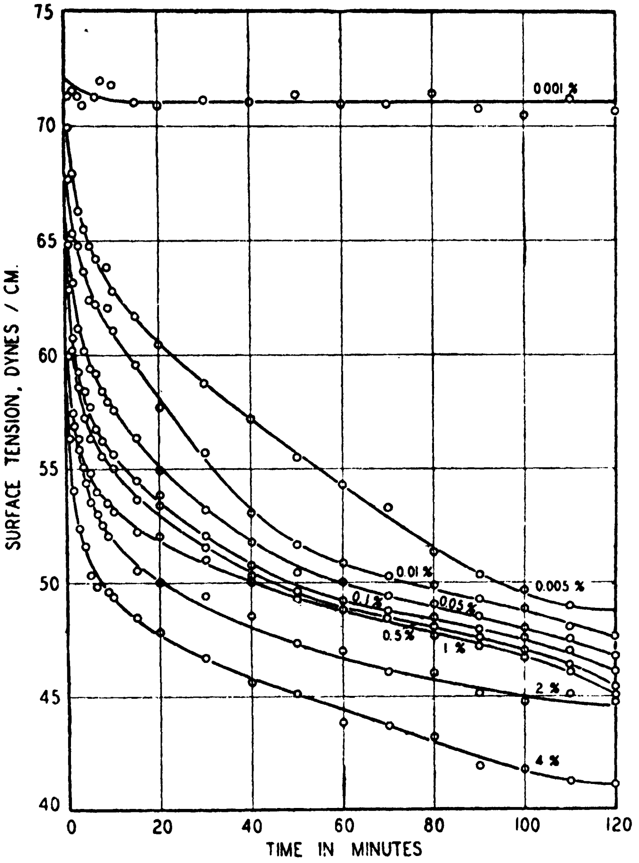

Fig. 1.

A long literature pertains to this subject, but recently Hauser and Swearingen[1] have re-examined very accurately by the photography of pendant drops (see p. 454) the surface tension of aqueous solutions of freshly dialysed egg albumin in conductivity water. Their graphical records are of great interest and we reproduce three (Figs. 1, 2 and 3).

The authors observed that solutions containing from 0·005 to 2 per cent. of albumin tend toward the same limiting values of σ after extensive ageing. Solutions with higher or lower albumin content approach different limiting values of σ. It is inferred that the responsibility for the prolonged ageing effect is the formation of secondary multilayers under the primary surface film.

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[1] *J. Phys. Chem.*, **45**, 644 (1941).

The surface tension of freshly formed solutions is profoundly influenced by the albumin concentration of the solution, with diminishing effects as the age of the surface increased. The greater time required for the formation of secondary layers in the more dilute solutions is reflected in the occurrence of broad plateaus in the σ/concentration curves of the younger surfaces and the later shortening and shift of the plateau into the weaker concentration range with older surfaces.

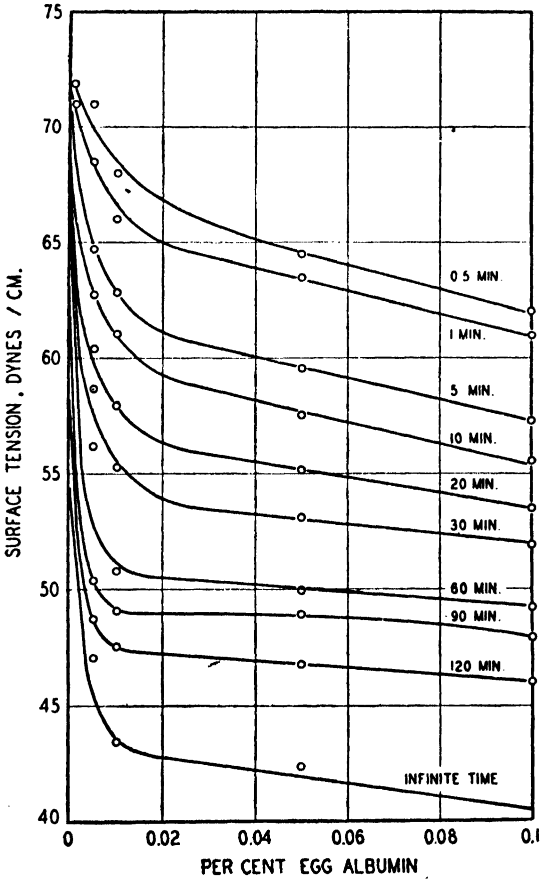

Fig. 2.

With solutions of 0·005 per cent. concentration the surface tension is considerably affected by the pH value and the degree of surface ageing. In the isoelectric zone a minimum surface tension is exhibited by surfaces at all ages ; a maximal value of σ appears in the slightly aged solutions at about $p\text{H} = 8{\cdot}5$. This maximum disappears with longing ageing and σ rises, commencing at the isoelectric zone and continuing through the pH range on the alkaline side. A sharp maximum develops in the acid range at about $p\text{H} = 2{\cdot}5$, followed by a decrease in σ at still lower pH values. The authors interpret the *p*H effect on ageing and surface tension in terms of the manner in which acid and alkali influence the ionic state of the solute and the rate of film formation, coagulation, and spreading. Salt formation and salt dissociation are involved as well as the rate of denaturation and coagulation in the surface layers.

Whilst flask ageing for 56 hours produced but little effect on the

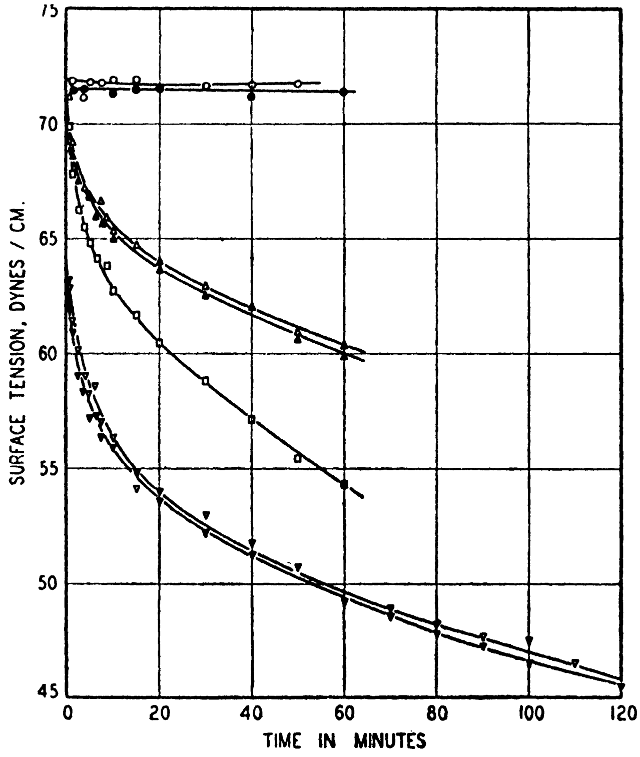

Fig. 3.

ageing and surface tension of a 0·5 per cent. solution of egg albumin, the mechanical agitation of 0·005 per cent. solution produced incipient coagulation of much of the albumin (see p. 28 and p. 433). Equilibrated and non-equilibrated samples exhibit the same slight ageing characteristics. Similarly was the influence of heating for 3 hours at 60° C. a solution of 0·005 per cent. concentration. Heat-coagulated albumin is insoluble, has no tendency to redissolve and spreads slowly, if at all.

FILM FORMATION AT THE GAS/LIQUID INTERFACE

Rayleigh's view that films can form on the surface of certain solutions has been amply confirmed by numerous workers. Rhode[1] demonstrated the growth of films on the surface of aqueous solutions of dyes, whilst Ghosh and Nath[2] have extended his work to include many complex organic substances, treating the formation of films on the basis of diffusion of molecules into the surface and their condensation therein.

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[1] *Ann. Physik.*, (iv.), **19**, 935 (1906).

[2] *J. Phys. Chem.*, **36**, 1916 (1932).

The existence of films built up by adsorption is especially demonstrated in froths or foams and in the study of bubbles.

Plateau[1] recognised that in bubbles and foams the two chief factors necessary are a certain degree of viscosity of the liquid used and a low air/liquid surface tension. The former tends to resist thinning of the liquid films to the rupture point, whilst a low surface tension is necessary, since surface tension is the chief active force promoting thinning. Soap solutions readily yield permanent foams owing to their low surface tension and their high viscosity. Plateau defined two viscosities for a liquid capable of frothing, the *internal viscosity* due to internal friction and the *superficial viscosity* which resists the movement of a body situated in the air/liquid interface. Stables and Wilson[2] confirmed the existence of this superficial viscosity in the case of a saponin solution which frothed readily.

Hillyer[3] determined the surface tension and foaming capacity of a number of solutions in an approximate manner and correlated the results with the viscosities of the solutions. He noted that high viscosity alone will not account for stable foams; the surface tension must be low. Thus, 50 per cent. aqueous glycerine or a 6 per cent. aqueous solution of gum acacia, each very viscous, but with relatively high surface tensions, do not yield peristent froths, whilst beer and milk, not so viscous, but with lower surface tension values, froth easily.

Many investigations have been concerned with the presence of films at a gas/liquid interface, but the well-known work of Ramsden will serve to illustrate the general phenomena involved.

Ramsden[4] showed that agitation of various protein solutions caused a separation of some of the solute in the form of fibrous or membrano-fibrous solids and, in some cases, *e.g.* egg-albumin " by purely mechanical means these free-surface coatings can be heaped up to form visible solid masses of protein which in some cases is not only ' de-soluted,' but at the same time coagulated and rendered permanently insoluble in the mother-liquid." He found that such " surface-coagula " could be separated from many protein solutions[5] and from certain colloidal solutions and suspensions, even when the concentration of solute was very small, in fact only 1 in 1,000,000. The separated solid possessed either a delicate membranous structure, a fibrous structure, or loosely contiguous particles.

Ramsden[6] observed in such solutions a typical Plateau surface viscosity, accompanied by a special superficial resistance to shear. "The molecules which stud the surface are in such close lateral continuity that they make it tangentially ' rigid.' " The time factor varied greatly with the type of system investigated. His earlier work records that "bubbles of solutions of egg-albumin, caseinogen and saponin exhibit remarkable phenomena, which show that the bubble film as a whole is very imperfectly elastic and is covered with solid membranes. Egg-albumin bubbles are deformed on collapse by the formation of persistent folds of solid protein in the bubble film. Bubbles of pure saponin solution, containing 0·01 per cent. or more of saponin, fall on collapse into innumerable shimmering folds containing isolated curved rods of *solid* saponin, although water is capable of dissolving at least 2,500 times this amount."

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[1] *Pogg. Ann.*, **141,** 44 (1870).

[2] *Phil. Mag.*, **15,** 406 (1883).

[3] *Phil. Mag.*, (5), **15,** 406 (1883). Cf. Luvini, *ibid.*, **40,** 190 (1870); Quincke, *Wied. Ann.*, **35,** 589 (1888); Rayleigh, *Proc. Roy. Inst. Gt. Brit.*, **13,** 85 (1890); Schutt, *Ann. d. Physik.*, (4), **13,** 712 (1904); Johlin, *J. Biol. Chem.*, **84,** 543 (1929).

[4] *Arch. Anat. Physiol.*, 517–534 (1894); *Z. physik. Chem.*, **47,** 336 (1904); *Trans. Liverpool Biol. Soc.*, **33,** 3 (1919). See also Hall, *Proc. Roy. Soc. (Dub.)*, **9,** 56 (1899); Benson, *J. Phys. Chem.*, **7,** 532 (1903); Zawadzki, *Z. physik. Chem.*, **35,** 77 (1900); **42,** 612 (1903); Metcalfe, *ibid.*, **52,** 1 (1905); Rhode, *Drude's Ann.*, **19,** 935 (1906).

[5] See Schmidt, *J. Hyg.*, **14,** 399 (1914).

[6] *Trans. Faraday Soc.*, **26,** 796 (1930).

(Obviously such solid matter must raise the stability of a bubble. A coherent membrane is not essential as solid particles will also stabilise bubbles, since, as Ramsden has pointed out, they (1) serve as *points d'appui*, (2) oppose local disturbances of the film, (3) oppose such deformation of the surface as tends to expose a new surface with higher surface tension.)

It was recognised by Ramsden and confirmed by later workers [1] that his mechanical surface-coagula are the result of adsorption of solute at the air/liquid interface, with adsorbed molecules passing partly out of solution. Adsorption-surfaces which yield solid "massed adsorpta" are either extremely viscous (or even rigid), in which cases the adsorbed particles are in direct mutual contact, or they are freely mobile, the particles being then more widely spaced. Saponin and proteins yield rigid adsorption-surfaces, whilst quinine and soaps yield typical freely mobile adsorption-surfaces. "In the many cases where adequately durable bubble-films are obtainable, the interference colours developed as the film gets thinner are disposed in horizontal bands when the surfaces are mobile, but are disposed chaotically when the surfaces are rigid."

Although most "massed adsorpta" are completely resoluble, some, such as egg-albumin and fibrinogen, remain insoluble, a change "attributed to catalytic condensation of the close-packed specifically strained and orientated protein molecules into a single vast chemical aggregate."

In those systems where there is a surface-rigidifying solute and a non-solidifying solute capable of exercising a greater surface tension depression, the free surface is mobile, owing to the preferential adsorption (independent of concentration) of the more surface-active solute.[2]

Wilson and Ries [3] have published most interesting data relating to surface films and their rigidity. They point out that the collapse of a bubble results from the tendency of the solution to run down the bubble surface and thin out the film to breaking point, and hence some stabilisation of the film is required to resist the force of gravity or to prevent thinning by capillary forces. Film formation was studied at the air/liquid interface with soaps, saponin and other substances. A torsion pendulum apparatus was employed to measure accurately the superficial viscosity of the films. The results obtained with sodium stearate in aqueous solution showed: (i.) surface films even in the case of a 1 in 100,000 dilution are plastic solids and not viscous liquids, (ii.) a time factor enters into film formation, (iii.) higher concentrations of the soap build up films more rapidly and eventually give stronger films.

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[1] See especially Wu and Ling, *Chinese J. Physiol.*, **1**, 407 and 431 (1927).

[2] Cf. Rehbinder and Wenström, *Kolloid-Z.*, **53**, 156 (1930).

[3] *Colloid Symposium Monograph*, **1**, 145 (1923); also du Noüy, *J. phys. radium*, **6**, 145 (1923), and *Compt. rend.*, **174**, 962 (1922); Horn, *Am. J. Pharm.*, **98**, 53 (1926).

Sodium oleate gave evidence of marked adsorption at the air/liquid interface, but only in the case of more concentrated solutions ($>$ 1 in 5,000) was a plastic solid film formation made evident. Saponin showed a much better tendency to form films. The gradual growth of surface films was investigated by an ultramicroscopic analysis and the final thickness observed in the different solutions varied from 10 to 40 microns.

The experimental data was correlated with tests of foam-stability and the conclusion reached that the main factor in producing persistent bubbles is not the surface tension [1] or the viscosity of a solution but the presence in the films of a "plastic solid surface," an opinion shared by Freundlich.[2]

FROTH OR FOAM

Froth or foam is the more or less stable extended air/liquid interface arising when bubbles persist at the surface of a liquid due to agitation, aeration or ebullition. An enormous film-surface of liquid is presented to the gas phase, so that foam is primarily a labile system owing to the tendency for the interface to be reduced to a minimum.[3]

Evanescent foams are formed when certain aqueous solutions of inorganic compounds, *at certain concentrations*,[4] are agitated. Thus, a 3 per cent. NaCl solution on shaking produces a temporary foam, as does also 90 per cent. aqueous H_2SO_4. Again, certain organic liquids such as acetic acid will permit frothing in aqueous solution. *No pure liquid will yield a persistent foam*, cessation of agitation leading to the immediate subsidence of those bubbles which may have formed.

The more persistent froths result when aqueous solutions of such compounds as saponin, soap, proteins, rennet, etc., are agitated, and in each instance it can be demonstrated that the solute markedly reduces the surface tension of water. There is, however, no relation between the surface tension of a liquid and the *size* of the bubbles obtained therefrom, but the viscosity is a definite factor in this connection.[5] The explanation of frothing is based on surface tension considerations.

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[1] Ostwald and Steiner, *Kolloid-Z.*, **36**, 342 (1925).

[2] "Colloid and Capillary Chemistry" (London, 1926), p. 790.

[3] For detailed discussions on various aspects of foams see Desch, *J. Inst. Metals*, **11**, 57 (1914); **22**, 241 (1919); Boys, "Soap Bubbles" (London, 1924); Wells, "Surface Films" (London, 1930); Clayton, *Ind. Chemist.*, **1**, 489 (1925); Foulk, *Ind. Eng. Chem.*, **21**, 815 (1929); Ostwald and Meissner, *Kolloidchem. Beihefte*, **26**, 1 (1928); Rehbinder and Wenström, *Kolloid-Z.*, **53**, 145 (1930); Edser, *Brit. Assocn. Colloid Repts.*, **4**, 314 (1922); Talmud and Sukhovolskaya, *Z. phys. Chem.*, **A. 154**, 277 (1931); Aleinikov, *Koll. Beihefte*, **36**, 82 (1932); Rudolph, *Kolloid-Z.*, **60**, 308 (1932); Dumanskii, Granskaya and Novikov, *Schriften zentral. biochem. Forschungsinst. Nahr.-Genussmittelind.* (*U.S.S.R.*), **3**, 361 (1933); Remy and Seeman, *Kolloid-Z.*, **72**, 3 (1935); Berkman and Egloff, *Chem. Reviews*, **15**, 377–424 (1934); Schnurmann, *Kolloid-Z.*, **80**, 148 (1937); Auerbach, *ibid.*, **80**, 27 (1937); Sasaki, *Bull. Chem. Soc. Japan*, II., 797 (1936); **13**, 517; 669 (1938); **14**, 3; 63; 107; 250 (1939); Knöll, *Kolloid-Z.*, **86**, I (1939); Trapeznikov, *Acta Physicochim, U.R.S.S.*, **13**, 265 (1940).

[4] Cf. Foulk, *Kolloid-Z.*, **60**, 115 (1932).

[5] Schnurmann, *Z. physik. Chem.*, **Abt. A.**, **143**, 456 (1929); cf. Weichherz, Bodea and Nord, *ibid.*, **150**, 1 (1930).

SURFACE TENSION AND FROTHING

The Gibbs equation connecting the surface excess of solute (Γ) at an interface with the surface energy is

$$\Gamma = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}$$

where σ = surface tension, and c = equilibrium concentration of solute in solution.

Edser[1] has pointed out that frothing accompanies the agitation of a solution when $-c\frac{d\sigma}{dc}$ has a finite value, negative or positive. For 3 per cent. NaCl solution, to instance an evanescent froth, $d\sigma/dc$ is positive and small and for $-c\,d\sigma/dc$ to be finite, c must be large. For those solutes which enhance stable foams, $d\sigma/dc$ has a large negative value, so that $-c\frac{d\sigma}{dc}$ is large, although c may be very small.

Accordingly, since the coalescence of bubbles in a liquid occurs when the bubbles approximate close enough so that the liquid between them is sucked out, such coalescence cannot be avoided in a pure liquid. Some solute must be present, and even then $-c\,d\sigma/dc$ should not be very small or equal to zero, since this would produce conditions similar to those obtaining in pure liquids. It is obvious that, in order to avoid coalescence of the bubbles, the constitution of the solution must be different in the space separating the bubbles to that in the main bulk of the solution. Such a state of affairs only obtains when $-cd\sigma/dc$ has a finite value, positive or negative. As Bancroft[2] emphases, the *sine quâ non* for foam formation is the existence of a distinct surface film concentration gradient, *i.e.*, the concentration in the surface layer must differ perceptibly from that in the bulk of the liquid. Either negative or positive adsorption must occur at the air/liquid boundary or bubble walls.

Detailed investigation of the interdependence of the differences between static and dynamic surface tension, foaming and the tendency towards film formation of solutions has been reported by Foulk.[3] By studying the behaviour of two bubbles when contacted he observed that "in water or other pure liquids the bubbles coalesce at once on touching each other, thus giving a direct proof that under these conditions two approaching liquid surfaces continue the movement towards each other till the intervening layer of liquid breaks. If some salt is now added in gradually increasing concentration, it is found that the percentage of film formation (failures to coalesce) also gradually increases till it is nearly 100 per cent. Furthermore, film formation is promoted by both positively and negatively adsorbed substances." Thus, whilst aqueous saponin solution of 10 p.p.m. showed 49 per cent. film formations, when the concentration of saponin was 100 p.p.m. this percentage rose to 97·8. The following table by Foulk and Miller is of much interest, since it confirms the application of the theory of film formation in those peculiar cases of solutions of substances which only froth at certain concentrations.

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[1] *Loc. cit.*

[2] "Applied Colloid Chemistry" (New York, 1926), p. 364.

[3] *Ind. Eng. Chem.*, **23**, 1283 (1931); *Kolloid-Z.*, **60**, 115 (1932); *Ind. Eng. Chem.*, **24**, 277 (1932); **31**, 722 (1939). See Brown, *J. Am. Chem. Soc.*, **55**, 4521 (1933), on the surface tension of film-covered liquids.

TABLE 1

RELATION OF STATIC AND DYNAMIC SURFACE TENSION DIFFERENCES TO FOAM-ZONE HEIGHTS IN AQUEOUS SOLUTIONS OF SULPHURIC ACID

HS_2O_4.	Surface Tension.		Difference.	Foam-Zone Height.
	Static.	Dynamic.		
(per cent.).	(dynes/cm.).		(dynes/cm).	(cm.).
10	73·5	72·3	1·2	2·4
20	74·7	72·5	2·2	4·8
30	75·9	72·5	3·4	3·8
35	76·0	72·9	3·1	2·2
40	76·2	73·4	2·8	1·8
45	76·3	75·4	0·9	1·1
50	76·0	75·6	0·4	2·0
55	75·5	74·8	0·7	3·1
60	75·6	73·5	2·1	4·2
65	75·0	72·6	2·4	3·9
70	73·8	72·4	1·4	2·2
73	72·4	72·3	0·1	1·2
80	69·3	72·1	—2·8	3·6
90	?	66·3	?	6·2
96	57·9	63·1	—5·2	6·0

Bartsch[1] has carried out a very extensive investigation on foam systems. He found the significant fact that in two-phase foaming systems, the duration of the foam depends on the concentration of foaming agent present, this duration being a distinct maximum at low concentrations. Thus, taking the fatty acid series as an example, Bartsch gives the following data (see Table 2, p. 23).

From these and many other results it is evident that the maximum persistence of froth is greater, the lower the surface tension of the solution exhibiting maximum frothing. In the case of concentrated solutions the influence of surface activity is not supreme, as solubility and degree of dispersion must be considered. For example, the higher members of homologous series of surface-active substances possess smaller foam-forming capacities than the middle members. The higher the member in the series, the greater is the content of the solution in respect to

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[1] *Kolloidchem. Beihefte*, **20**, 1 (1925); see also the very interesting experiments by Rehbinder and Wenström, *Kolloid-Z.*, **53**. 145 (1930).

TABLE 2

OPTIMUM FROTH-FORMATION OF FATTY ACIDS IN WATER

Acid in Solution.	Maximum Duration of Froth.	Concentration of Acid at this Maximum.	Surface Tension of Solution at this Maximum.
	Seconds.	Mol./litre.	Dynes/cm.
Formic	4	0·45	70
Acetic	8	0·20	69
Propionic	11	0·25	61
Butyric	18	1·0	33
Valeric	9	0·015	64
Capronic	13	0·0075	57
Heptylic	16	0·0015	60
Caprylic	12	0·00025	66
Nonylic	5	0·00007	70

submicrons, and submicrons alone are unfavourable to foams.[1] Increasing the *molecular* solubility of a surface-active substance raises its foaming power, *e.g.*, dissolving nonylic acid in 60 per cent. aqueous ethyl alcohol.

Bartsch emphases that solutions of surface-active substances give better foams, the steeper the concentration gradient between the Gibbs adsorption layer and the solution and the greater the heterogeneity of this layer.

Dealing with the presence of solid particles entangled in foams (three-phase systems) Barsch shows that the stability of the foam depends upon (1) the concentration of the frothing agent, (2) the affinity of the frothing agent and the solvent for the solid phase, (3) the degree of dispersion of the solid phase. Regarding the last factor, he states that solids of fine dispersion enhance the duration of foam much less than do solids of much coarser dispersion. In the dispersion range between colloidal solution and coarse suspension there is an optimum degree of dispersion corresponding to maximum foam persistence.[2]

Ostwald and Steiner [3] expressed the view that there is no necessary relation between foaming power and reduction of surface tension, and to this Bartsch [4] takes exception. Determining the surface tension curves and foam stability-concentration curves for certain alcohols and fatty acids in aqueous solution he finds the foam stability increases to a maximum (coinciding with maximum depression of surface tension) and then rapidly decreases, *i.e.*, foaming power diminishes completely at sufficient concentration of the surface-active solute. Bartsch explains this on his heterogeneity theory which correlates maximum foaming with equal numbers of solvent and of solute molecules in the surface layer.

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[1] Cf. Traube and Klein, *Kolloid-Z.*, **29**, 236 (1921).

[2] Alexander speaks of a zone of maximum colloidality, *J. Am. Chem. Soc.*, **43**, 434 (1920); *Kolloid-Z.*, **36**, 334 (1925).

[3] *Kolloid-Z.*, **36**, 342 (1925).

[4] *Ibid.*, **38**, 177 (1926).

Steep concentration gradient is fundamental to the formation of foam and subsequent heterogeneity, *e.g.*, by the presence of de-soluted material, increases stability. It is necessary to bear in mind the conditions necessary for foam formation and the conditions influencing the *properties* of the foam, *e.g.*, its stability. Thus, sodium cholate solutions yield a foam and its stability may be enhanced by solids. Addition of (say) $CHCl_3$, which sets the solid better than does water, will cause collapse of the foam.

POLAR GROUPS AND FOAMING CAPACITY

Talmud and Suchowolskaja[1] have investigated the formation of "elementary foam." They find that more or less stable foams are possible with aqueous solutions of surface-active substances, when these solutions possess a low surface tension and a low vapour pressure. Particularly stable foams result when the surface-active substance yields a viscous, amorphous-solid surface film.

Referring to Bartsch, when he says that foaming is better when there is a steeper gradient between the Gibbs layer and the solution (and the more heterogeneous this layer), they point out that his experiments concerned shaking solutions in closed vessels. Thus, Bartsch shook solutions with air saturated with the vapour of the solution and under conditions excluding evaporation from the bubble walls. Their method was to release air bubbles of about 1·5 mm. diameter below the surface of the solution and note the time of persistence at the liquid surface in an *open* vessel. On the cleaned surface of pure water the bubbles burst immediately.

Insoluble films of surface-active substances were prepared on the surface of water by the technique of volatilisation of solvent from a solution of the material in an organic liquid. Thus, the surface films of insoluble surface-active palmitic, stearic and oleic acids were studied, as well as of cetyl alcohol and ethyl oleate. Twenty successive bubbles were observed and the mean life determined. In the case of pamitic acid, as an example, the data obtained were :—

Area covered in 10^{-10} Mol./cm.^{2}.	Mean Stability of Bubble in Seconds.
0·0—3·06	0·0
3·06	3·4
3·16	3·3
3·25	3·15
3·4	2·33
3·7	1·5
4·2	0·8
4·9	0·6
5·4	0·5
7·9	0·0

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[1] *Z. physik. Chem.*, **154**, 277 (1931). The present account translates the main features of their text.

Where the insoluble films are formed from substances of high boiling point and very low vapour pressure evaporation does not influence the stability of the elementary foam. In the case of readily liquid, soluble surface-active substances, the surface layer can rapidly become poorer through evaporation, diffusion failing to restore the volatile substance; the foam stability is affected. Again, at certain concentrations, there is a greater evaporation of water than of the surface-active material. The following data in Table 3 refer to foam due to solutions of ethyl alcohol in water.

TABLE 3

EFFECT OF EVAPORATION ON FOAM STABILITY IN AQUEOUS SOLUTIONS OF ETHYL ALCOHOL

Evaporation permitted.		No Evaporation permitted.	
Alcohol Concentration (Weight per cent.).	Stability of Bubble in Seconds.	Alcohol Concentration (Weight per cent.).	Stability of Bubble in Seconds.
0·25	1·1	0·3	0·0
1·0	1·46	1·0	6·5
2·5	22·4	3·0	15·0
5·0	26·9	6·0	4·0
10·0	24·7	12·0	0·5
25·0	24·1	24·1	0·0
30·0	67·6	30·0	0·0

It will be observed that the two cases differ entirely.

The molecular-physical picture of the process of alteration of bubble stability is related by Talmud and Suchowolskaja to the thickness of the insoluble surface-active skin.[1] An air bubble deep below the surface of the solution which yields an insoluble skin of surface-active substance is not surrounded by an adsorbed film. It rises towards the free surface surrounded by an envelope of water. In such a bubble the air pressure p exceeds atmospheric pressure and $p = \frac{2\sigma}{r}$ where $\sigma =$ the surface tension of the solution and $r =$ the radius of the bubble. If the bubble rises into the skin of surface-active material, it becomes thickened, and at the point of contact the surface tension decreases and the pressure difference becomes $\Delta p = \frac{2\Delta\sigma}{r}$, where $\Delta\sigma =$ the decrease in surface tension. Under the influence of this pressure difference at the place of contact of the bubble with the surface film, the bubble bursts. Bubble stability is only ensured if the tensile strength of the surface film is greater than the pressure difference which causes bubble bursting.

The authors believe that the tensile strength of the surface film is connected with the degree of hydration of its polar groups. At that thickness of the surface film when its molecules are arranged horizontally and are not oriented, *i.e.*, when the surface tension is that of pure water, there is little hydration of the polar groups. In the saturated adsorption layer (surface tension now minimal) the degree of hydration of the molecules of the surface-active material reaches a certain maximum, which corresponds to the thickest packing of the molecules or micelles[1] in the surface layer.

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[1] Cf. Hardy, *J. Chem. Soc.*, **127**, 1 (1925).

It is emphasised that the hydration maximum of the polar groups of the molecules or micelles of the surface-active substance lies between two minimal hydration values. The strongly hydrated polar groups resemble the hydrated micelles of lyophilic colloids. In the region of maximum hydration of the polar groups, the molecules are oriented, inclining at a certain angle to the surface, and interlacing each other, form a kind of gel structure. The minimal hydrated surface-active films represent in the saturated adsorption layer a layer of pure surface-active substance, of which the surface tensile strength (*e.g.*, in the case of a liquid) must, as with pure water, equal *nil.*

When the degree of hydration of the molecules of the surface-active substance in the adsorbed layer, due to the approach to complete orientation of the molecules, begins to fall, then the tensile strength of the surface skin begins to diminish. In concentration regions where the adsorbed layer of the surface is not yet saturated, the air bubble, which forms in the solution is surrounded by an adsorbed skin which also is not saturated. When the ascending bubble reaches the surface of the solution, there is formed at the place of contact of the bubble and the surface layer a layer of greater concentration of surface-active material, nearer to saturation. That is, at the place of contact, the surface tension falls ($\Delta\sigma > 0$) and there is developed a pressure excess Δp.

In the special case when the surface tension of the solution is greater than that of water, as with non surface-active electrolytes, at the contact of bubble and surface layer (which consists of more or less completely oriented water molecules), there is no alteration of surface tension and no pressure difference. Hence, increase in concentration of the negatively adsorbed substance means a gradual increase in bubble stability or, on reaching the maximum, it remains constant and does not decrease.

Besides the degree of hydration of the polar groups in the adsorption layer and its tensile strength controlling the opportunity for stable elementary foam, there is another factor which regulates the stability of individual bubbles. This factor is the draining velocity of the water layers in the bubble walls. Such draining velocity is greater, the longer the chain of polar molecules in the adsorbed layer and the less soluble the surface-active substance. Polar molecules with short chains (readily soluble) are strongly hydrated and therefore more strongly bound with the deeper-lying water layers of the bubble walls. Polar molecules with longer chains (difficult solubility) appear less hydrated and, in consequence the deeper-lying water layers meet with less resistance to draining. Thus is explained the fact that surface-active substances with long chains which are poorly soluble form bubbles with a relatively greater tensile strength of the adsorbed layer and yet of lesser stability, whilst readily soluble surface-active substances (short chains) yield bubbles of relatively less tensile strength in the adsorbed layer, but of greater stability.

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[1] Cf Zocher and Stiebel, *Naturw.*, **17**, 672 (1929).

Many aspects of the behaviour of foams have been investigated, such as the mechanical properties,[1] the viscosity,[2] adsorption phenomena,[3] and the measurement of foam stability.[4]

THE UNIT OF FOAMINESS

Bikerman [5] has established foaming capacity as a physical quantity having the dimension of time and largely independent of the apparatus or technique employed.

A measured volume of air (about 1,000 c.c.) was forced through a porous glass membrane and an overlying solution so that foam collected in a calibrated tube above. The average foam height was measured directly. It was noted that the foam volume was more general than the foam height and the average foam volume was proportional to the rate of streaming of the air. If v is the average foam volume and V the volume of air forced through the septum in t sec. then $\frac{vt}{\mathrm{V}} = f$, where f is a factor independent of the rate of streaming. Except for very large durations vt/V is practically constant. Moreover, vt/V is independent to the air pressure and the porosity and size of the septum. The value of vt/V tends to a limit when the amount of superimposed liquid increases.

Bikerman, therefore, concludes that vt/V is the "natural" unit of foaminess. In the C.G.S. system it is of the dimension of the second. The symbol he suggests is Σ (from *Σάηωνος* =lather) and Σ is the limit of at large amounts of liquid. "It is readily seen that f is the life-time of a bubble in the foam. If the linear velocity of the air in the foam is u and the height of the foam layer h, this time is h/u. On the other hand, $u = \mathrm{V}/t\mathrm{Q}$, Q being the cross-section of the measuring tube, and $h = v/\mathrm{Q}$; hence $h/u = vt/\mathrm{V} = f$. This is the physical meaning of f; and all the rules announced for f apply to the life-time of a bubble."

Clark and Ross [6] have presented a thorough account of the measurement of static and dynamic foams in characteristic units, their aim being to establish a unit for *static* foams comparable to the Bikerman unit for *dynamic* foams and, if possible, to correlate the methods. The attempt to evaluate the average life of a bubble in a static foam can be made for any system in which the rate of collapse is known or where sufficient data are available to enable its calculation.[7]

[1] Siehr, *Kolloid-Z.*, **77**, 27 (1936); **78**, 156 (1937); **85**, 70 (1938).

[2] Sibree, *Trans. Faraday Soc.*, **30**, 325 (1934).

[3] Schütz, *Nature*, **139**, 629 (1937).

[4] Blom, *J. Inst. Brewing*, **43**, 251 (1937); van der Westlaken and McCormack, *Am. Brewer* **69**, (vii), 24 (1936); Weininger, *Wochschr. Brau.*, **49**, 273 (1932); Ross and Clark, *Communications: Wallerstein Labs.*, **6**, 46 (1939); Gray and Stone, *ibid.*, **10**, 159 (1940); Lederer, *Seifensieder-Ztg.*, **63**, 331 (1936); Helm and Richardt, *J. Inst. Brewing*, **42**, 191 (1936); Ostwald and Siehr, *Kolloid-Z.*, **76**, 33 (1936); **79**, II (1937); *Chem. Ztg.*, **61**, 649 (1937).

[5] *Trans. Faraday Soc.*, **34**, 634 (1938).

[6] *Communications: Wallerstein Labs.*, **6**, 46 (1939).

[7] Aleinikov, *Kolloid Beihefte*, **36**, 82 (1932).

During the course of their work it was noted that measurements of dynamic foams of egg albumin showed that CO_2 foam had a higher value for ϵ than air foam, but the reverse was the case for static foams. It is argued, with evidence from a number of other investigators that in the case of air foams, only denaturation of the surface egg albumin appears to take place. With CO_2 foam, however, there is a reaction between the gas and the protein, the foam comprising very fine bubbles breaking rapidly and leaving a coagulated residue. It is not to be expected, therefore, that the value for the average life of foam bubbles would remain constant whether the measurements be made by a static or a dynamic foam meter. Foaminess as measured by the static foam meter is based on the rate of decomposition of the foam ; in the case of the dynamic foam meter the measurement depends upon an equilibrium between the rates of formation and decomposition. Aleinikov [1] pointed out that the coagulation of a dynamic foam involves the rupture of newly-formed surfaces, whereas the coagulation of a static foam involves the rupture of surfaces which have had time to age and are actually ageing during measurement.

EGG WHITE FOAM

Amongst the important foams involved in emulsion studies two demand special attention : beaten egg white and milk froth. Their importance lies in the incidence of protein denaturation, which can adversely affect emulsion stability when certain emulsions are subjected to agitation, including simple transport by road or rail. Musher's patent [2] for excluding the air space of bottles of salad dressings by means of paraffin wax is based on sound considerations.

Investigations on the foaming of egg white solutions when agitated have been made by Barmore,[3] Chang and Hsieh,[4] and St. John and Flor.[5] All agree that the protein is adsorbed at the air/water interface. Acids and acid salts increase considerably the foam stability, whilst egg yolk reduces the foaming tendency. The thin or watery part of the white gives a larger volume and has a more defined texture when beaten than the thick portion of the white. Optimum frothing results if the egg white is chilled to about 18° C. before beating.

Quantitative experiments by Henry and Barbour [6] studied the effects of rate and time of beating, temperature, *p*H value, the addition of water and oil, and the defrosting of stored white. Their results are accompanied by photographs of the foams produced. When using dried egg white as the solute in solutions of egg white there appears to be a necessity for a preliminary slight fermentation of the white in order to produce substances which markedly favour frothing.[7]

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[1] *Kolloid Beihefte*, **36**, 82 (1932).

[2] U.S. 1,782,011 (1930).

[3] Colo. Agr. Expt. Sta., *Tech. Bull.*, **9**, 58 pp. (1934).

[4] *J. Chinese Chem. Soc.*, **2**, 117 (1934). See also Jochims, *Kolloid-Z.*, **43**, 361 (1927) on a method of measuring the spinning power of egg white.

[5] *Poultry Sci.*, **10**, 71 (1931).

[6] *Ind. Eng. Chem.*, **25**, 1054 (1933) ; cf. Peter and Bell, *ibid.*, **22**, 1124 (1930).

[7] Cf. Cortese, *Ann. sper. agrar.*, **3**, 125 (1930) ; Rahn, *Food Inds.*, **4**, 300 (1932) ; Farrall, *ibid.*, **4**, 378 (1932).

An interesting investigation by Miss Bailey[1] has dealt with the foaming of egg white, using a Hobart mixer in order to secure a hypocycloid whipping action. Unfrozen whites and thawed whites after frozen storage for short periods of time showed no pronounced difference in foaming power. Thick white exhibited a greater foaming capacity than thin white. Untreated egg white possessed a higher foaming capacity than did white acidified with phosphoric acid (*p*H 5, 6 and 7) or made alkaline with anhydrous sodium carbonate (*p*H 9·5).

Specially to be noted in relation to such edible emulsions as salad dressings and mayonnaise are the results when oil was present. Added yolk diminished the foaming capacity of egg white and so did olive oil, but to a greater degree. Thus olive oil inhibits foaming capacity to a greater extent than yolk oil or, assuming that the two oils have equal effects, the yolk possesses some substance which tends to offset the inhibiting effect of the yolk oil.

Soybean proteins provide a suitable substitute for egg white in the preparation of edible emulsions. Solvent-extracted soybean flour dissolved in water whips to a stiff foam greatly resembling that of egg white.[2] Foaming is best in concentrations of 7 to 8 per cent. and at *p*H values far removed from the isoelectric point of *p*H 4·1. The presence of up to 2 per cent. of NaCl is beneficial. The optimum whipping temperature is 50° C.

MILK-FROTH

New milk readily froths, *e.g.*, after just drawing, on stirring or pumping, and on passage through a cream separator. Agitation of milk results in the creation of an extended air/liquid interface at which adsorption of the nitrogenous colloids[3] of the milk takes place. The bubbles show considerable permanence, no doubt due to the effect of denatured protein (as revealed by King[4] in his microscopic examination of milk froths in reflected light). Quantitative proof of protein accumulation in the froth has been given by Siedel and Hesse,[5] and by Leviton and Leighton.[6]

Froth allowed to remain undisturbed on milk gradually collapses, and eventually wrinkles of delicate, membrano-solid character lie on the surface. Brouwer[7] claims to have proved the existence in milk of peculiarly-shaped small bodies, which were membranes originally formed by adsorption of protein on gas bubbles and remaining in the milk after the bubbles have collapsed. Fig. 6, reproduced from Rahn,[8] shows the membranes after the collapse of milk froth from a separator.

Rahn showed that the addition of 0·5 per cent. of peptone to the milk altered the character of the milk froth, bubbles forming which burst in upon one another, gradually uniting to larger and larger bubbles. This is due to the change in character of the bubble walls, which are solid in the air phase, but redissolve in the liquid phase. Addition of gelatin to the peptone-milk causes still further change owing to the displacement of the peptone by the gelatin. The outer walls of the bubbles are now only semi-solid, and slow collapse of the bubbles follows the occurrence of rents in the walls.

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[1] *Ind. Eng. Chem.*, **27,** 973 (1935).

[2] Miss Monaghan-Watts, *Ind. Eng. Chem.*, **29,** 1009 (1937).

[3] Ansbacher, Flanigan and Supplee, *J. Dairy Sci.*, **17,** 723 (1934); Sharp, Myers and Guthrie, *ibid.*, **19,** 655 (1936); Webb, *ibid.*, **24,** 829 (1941).

[4] *Milchwirtschaft. Forsch.*, **15,** 103, (1933).

[5] *Molkerei-Ztg.* (*Hildesheim*), (1900), p. 638.

[6] *J. Dairy Sci.*, **18,** 105 (1935).

[7] *Niederlandsch. Tijdschr. Geneeskunde,* **67,** 409 (1923); also Hekma and Brouwer, *Verslag. Land. Onderzoek. Rijkslandbouwproefsta,* **18,** 46 (1923).

[8] "Physik der Milchwirtschaft" (Berlin, 1928), p. 6.

Siedel found that churning milk at a low temperature for about 45 minutes inhibited froth formation when the milk was subsequently passed through a cream separator. Cooling the milk without churning did not affect froth formation. Also, separated milk, cooled and churned, and then mixed with cream, frothed as usual when passed through a separator. Two facts emerge from these experiments: (*a*) churning fat-poor milk renders the colloid inactive, (*b*) the greater portion of the foam colloid is in the cream. Churning skim milk causes frothing with the consequent irreversible coagulation of the milk colloids. Thus, the cause of frothing being removed, later agitation has no effect. Cream is rich in milk colloids owing to the marked adsorption occurring at the enormous fat/water interface.

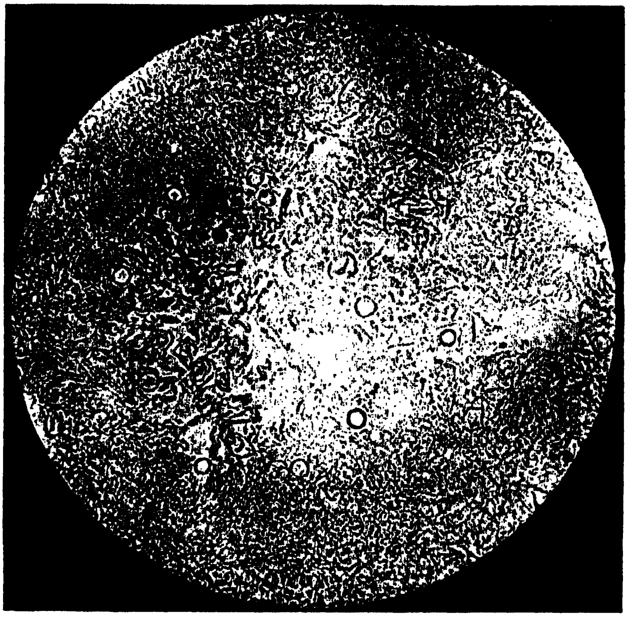

FIG. 4. Membranes from collapsed milk froth (Rahn).

An investigation of the phenomenon of foaming in relation to the temperature and the surface tension of milk has been made by Mohr and Brockmann.[1] They found that there is a definite connection between foam-solidity and surface viscosity. In general, milk gives a more stable foam, the greater the tendency to form a filmed surface, and there is an optimum surface viscosity relative to foam stability. The influence of temperature is different in different samples of milk, and the optimum temperature for frothing lies within the range 30°—60° C. Leete[1] finds that the tendency of milk to foam is at a minimum between 20° and 30° C. Below 20° C. foaming increases, whilst above 30° C. the foaming tendency rises rapidly. Rahn[2] observed that agitation (constant degree) of skim milk at different temperatures shows a rapid fall in foam tendency as the temperature increases. The graph connecting foam-height with temperature shows an inflexion point, the origin of which is not clear. He reports that the foam on warm milk is quite different to that on cold milk, the latter foam remaining unaltered for a short while and then collapsing suddenly. The warm foam collapses slowly at constant velocity. Again, the foam on new milk differs considerably from that on skim milk. The former is dull-looking with large bubbles, more like dough, whilst the latter is fine-grained and stiffer, resembling whipped egg white.

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[1] *Milchwirtschaft. Forsch.*, **11**, 48 (1930).

It is most probable that the skin which forms on heated milk[3] is also due to the colloid concerned in milk foam, the thin delicate skin being already present on the surface of the cold milk and becoming concentrated upon evaporation.

In the case of milk a skin appears on the surface when vacuum evaporation is attempted at room temperature, or when normal heating above 50° C. occurs. It was formerly believed that the skin was entirely albumin, but Semlritzki[4] was able to remove successive skins to a total amount of 1·023 per cent. of milk, *i.e.*, to an amount exceeding the albumin content. Friese[5] obtained thirty successive membranes from 1 litre of milk at 100° C.

WHIPPED CREAM

Whipped cream is a special case of milk-foam, since cream is richer than milk in fat and proteins. The remarkable stability and the great viscosity of whipped cream are due to the cell-like structure imparted by the air bubble, whose walls are stiffened not only by the denatured protein but by the more or less solidified milk fat. The latter factor vanishes on heating and the whipped cream collapses, although some foam structure persists due to the protein present.

Mohr[6] has investigated the physico-chemical factors involved, pointing out that cream of the same origin and chemical analysis may possess physical differences affecting whipping capacity according as the fat globules are solid or liquid and homogenised, coarse-grained or clustered together. He quantitatively ascertained that the duration of whipping profoundly influenced the volume of the whipped cream, the volume rising rapidly to a maximum (in about 3 minutes in his experiments) and then falling slowly to the original volume. The maximum solidity of the foam did not coincide with the maximum volume, but occurred several minutes later and then fell with extreme rapidity, butter forming with excessive beating.

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[1] U.S. Dept. Agr., *circ.* No. **108** (1930). See also Sanman and Ruehe, *J. Dairy Sci.* **13**, 48 (1930); " Fundamentals of Dairy Science " (1928), p. 172.

[2] " Physik der Milchwirtschaft," p. 16.

[3] Hertz and Jamison, *J. Physiol.*, **27**, 26 (1901).

[4] *Pogg. Ann.*, **37**, 450.

[5] *Milchwirtschaft. Forsch.*, **1**, 316 (1924).

[6] *Molkerei-Ztg.* (*Hildesheim*), **39**, 259 (1925).

Dahlberg and Hening [1] have made an extensive investigation on the viscosity, surface tension and whipping properties of milk and cream. It was found that a good whipping cream invariably yielded a smaller volume when whipped than did poor whipping cream. Whipping capacity was improved by ageing of the cream, increase in fat content, and increase in solids-not-fat. In a general way, factors (excluding homogenisation) which increased the viscosity of cream also improved the whipping capacity. "The surface tension of milk and cream cannot be definitely related to whipping properties under all conditions, but the general relationship of decreased surface tension with improved whipping properties is true in the normal product."

The authors found that as the whipped cream began to stiffen, the fat globules became distorted and grouped into clusters, which appeared to be fairly uniformly distributed throughout the mass.

TABLE 4

EFFECT OF WHIPPING FOR VARYING PERIODS OF TIME ON SOME OF THE PROPERTIES OF WHIPPED CREAM

Whipping Time.	Stiffness.	Overrun.	Drain after 24 hours.	Fat in Drain.	Body of Whipped Cream.
Seconds.	Watts.	Per cent.	c.c.	Per cent.	
Start	125				
90	147·5	71·8	Too soft to remain on 12-mesh wire screen.		Too soft
105	155	75·6			„ „
120	165	79·1			„ „
135	182·5	85·6	57	6·84	Sl. too soft
150	225·0	94·8	37	2·19	Good
165	265·0	94·8	23	1·34	„
180	262·5	85·1	20	1·23	Sl. soggy
195	250·0	74·7	19	1·38	Soggy
210	250·0	68·5	16	1·52	„
240	240·0	57·3	18	1·25	Very soggy
300	230·0	35·5	27	1·17	Buttery

Sl. = Slightly.

They also observed that the whipping property of cream is increased as the percentage of fat present is increased. The probability that the clumping of the fat globules is a prominent factor in the structure and, therefore, the viscosity of whipped cream was experimentally demonstrated.[2] Pasteurisation of cream is known to reduce whipping capacity, and this fact is connected with the effect of pasteurisation in breaking up clusters of fat globules. Ageing of cream assists clustering and whipping. The source of the cream is important, as the larger the fat globules therein, the more readily does clumping occur.

Modern work on the whipping of cream has aimed at the quantitative evaluation of the stiffness of the foam. Templeton and Sommer[1] employed a turbine whipper driven by a motor of such power as to maintain a constant speed. The load on the motor and its rate of increase were noted at regular intervals. Mueller[2] used a mechanical whipper and sensitive wattmeter, thus obtaining a continuous record of the stiffness[3] of the cream throughout the whipping process by simply recording the input of the motor in watts at intervals of 10 seconds. Table 4 is reproduced from Mueller's report[4] and has much interest in relation to the problem of the formation of butter from cream (see p. 428).

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[1] New York (Geneva) Agr. Expt. Sta., *Tech. Bull.*, **113**, (1925).

[2] *Milk Plant Monthly*, **15**. (3), 77 (1926). See also Rahn and Sharp, "Physik der Milchwirtschaft" (Berlin), 1928, p. 141.

POLARISATION

Accepting the idea of an unbalanced condition of molecular forces and a capillary layer of a density different to that of the bulk liquid, then if the molecular forces in the capillary layer are selective towards the groupings in molecules, the conception of a capillary layer mechanically and electrically polarised readily follows.[5]

In 1912, Hardy[6] drew attention to the molecular architecture of surface films : " If the stray field of a molecule . . . be unsymmetrical, the surface layer of fluids and solids, which are close packed states of matter, must differ from the interior mass in the orientation of the axis of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways."

Independently of Hardy and of each other, Langmuir[7] and Harkins[8] arrived at the same conclusions regarding the structure of liquid surfaces and the nature of surface tension. The basic idea involved is that in the surface of a liquid in contact with air (or its own vapour) the molecules are orientated, and the main factor determining the surface tension is the structure of the surface layer of atoms. The surface molecules are so orientated that their most active portions are drawn inwards, so that the least active portions of the molecules (orientated towards the vapour phase) characterise the surface layer. The active portion of the molecule is considered to possess a strong stray field or residual valence, hence the molecules in a surface layer are packed in such a manner that this residual valence is a minimum. On this view, surface tension (or surface energy) is defined by Langmuir as "a measure of the potential energy of the electro-magnetic stray field which extends out from the surface layer of atoms. The surface energy of a liquid is thus not a property of the group molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer."

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[1] *J. Dairy Sci.*, **16**, 329 (1933) ; **17**, 307 (1934).

[2] *Ibid.*, **18**, 177 (1935).

[3] Attention is drawn to interesting work on the elastic properties of froth by Derjaguin, *Kolloid-Z.*, **64**, 1 (1933) ; **68**, 243 (1934).

[4] The cream used contained 33 per cent. of fat and was aged for 48 hours at 38° F.

[5] See Dorsey, *Bull. Nat. Research Council*, No. **69**, 60 (1929) ; Margenau, *Phys. Rev.*, **38**, 365 (1931).

[6] *Proc. Roy. Soc.*, **A.**, **86**, 634 (1912) ; **A.**, **88**, 330 (1913) ; *J. Gen. Physiol.*, **8**, 641 (1927).

[7] *Met. Chem. Eng.*, **15**, 468 (1916) ; *J. Am. Chem. Soc.*, **39**, 1848 (1917) ; Alexander's " Colloid Chemistry " (New York, 1926), Vol. I., 525 ; *Colloid Symposium Monograph*, **3**, 48 (1925) ; *Chem. Reviews*, **13**, 147 (1933) ; *Angew. Chem.*, **46**, 719 (1933).

[8] *J. Am. Chem. Soc.*, **39**, 354, 541 (1917) ; *Colloid Symposium Monograph*, **2**, 141 (1925) ; **6**, 17 (1928) ; Alexander's " Colloid Chemistry " (New York, 1926), Vol. I., 192 ; *Z. physik. Chem.*, **Abt.**, **A.**, **139**, 647 (1928) ; *Science*, **70**, 433, 463 (1929).

Thus in the liquid paraffin series of hydrocarbons the molecules are so arranged that the CH_3 groups at the ends of the hydrocarbon chains form the surface layer, no matter how long the chain may be. Experiment shows that the whole series, from hexane to molten paraffin, have practically the same surface energy, viz., 46 to 48 ergs/cm.[2], although their molecular weights greatly vary. Again, the total surface energies of the fatty acids quickly reach a series constant[1]; thus, formic $>$ acetic $>$ propionic $>$ butyric, but the value of the 4-C acid persists almost constant up to the 18-C acid. Stanley and Adams[2] have pointed out the general correlations between chemical structure and surface tension depressant action. For organic liquids in general the active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, are orientated towards the interior of the liquid, as also are groups which contain N, S, O, I, or double bonds. Langmuir's work on the surface films of organic liquids on water or mercury and Harkins' work on surface tension phenomena strongly support these ideas.[3] Over the past few years there has appeared a mass of literature demonstrating the importance in physical and biochemistry of the notion of orientation. An apt illustration pertinent to the study of emulsions is the investigation by Afanas'ev, Talmud and Talmud.[4]

These workers showed that when molten palmitic acid is sprayed, the cooled droplets have a surface which consists of methyl groups, whereas if the melted acid is emulsified in hot water and the emulsion is poured into cold water, the solidified globules have a surface with carboxyl groups. The two kinds of surfaces react quite differently quantitatively towards ammonia. As expected, mixtures of melted acid dissolved in paraffin wax prior to emulsification yield globules with varying amounts of carboxyl groups exposed in the surface.

Other interesting illustrative experiments are those of Merckel[5] on quantitative regularities in the surface tension of homologous series, Smith and Sorg[6] on the surface tension of aliphatic alcohols, and Gortner[7] on interfacial energy and the molecular structure of organic compounds.

PROTEIN MONOLAYERS ON WATER

Proteins are common emulsifying agents, especially in the preparation of edible emulsions. Attention is directed briefly to modern work on protein monolayers on water in view of the admitted importance of the head-space in vessels containing such emulsions, particularly during transport (see p. 433).

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[1] Hunten and Maass, *J. Am. Chem. Soc.*, **51**, 153 (1929); cf. Taylor and Boell, *J. Cellular Comp. Physiol.*, **3**, 385 (1933).

[2] *J. Am. Chem. Soc.*, **54**, 1548 (1932).

[3] See Adam, "The Physics and Chemistry of Surfaces" (Oxford, 1940); Rideal "Surface Chemistry" (Cambridge, 1932); Heymann, *Kolloid-Z.*, **57**, 81 (1931); Adam, Rideal, *et al.*, *ibid.*, **61**, 129 (1932).

[4] *Acta Physicochim. U.S.S.R.*, **5**, 853 (1936).

[5] *Proc. Acad. Sci. Amsterdam*, **38**, 387 (1935); *Kolloid Beihefte*, **45**, 413 (1937).

[6] *J. Phys. Chem.*, **45**, 671 (1941).

[7] "Selected Topics in Colloid Chemistry" (New York, 1937), Chaps. VI and VII.

Devaux [1] noted the coherent, elastically compressible film formed on the surface of clean water to which egg white was added and concluded that a single layer of molecules (monolayer) had formed at the surface. Many investigations have since been recorded and the student is recommended to read the summaries by Langmuir [2] (" Protein Monolayers "), Gorter [3] (" Protein-Films "), Mitchell [4] (" The Structure of Protein Monolayers "), and Schaefer [5] (" Expansion Patterns of Protein Monolayers on Water ").

Now familiar is the method of investigating protein solutions by forming a film on the surface of the aqueous solution contained in a suitable trough with apparatus for compressing the film quantitatively. Various methods exist for spreading the protein to a surface film.[6] The cause of spreading is the molecular arrangement involved which leads to the hydrophobic portions of the molecules of protein lying in the surface and the hydrophilic groups remaining in the water. An unfolding of the molecule is thus necessary. The outstanding characteristic of protein monolayers is their insolubility. They are also very elastic and compressible.[7]

When a glass or metal plate is dipped into a protein solution, then into a concentrated solution of a salt such as ammonium, sodium or magnesium sulphate, or sodium chloride, a compact film of protein often 200–1,000 Å thick is salted out onto the plate. This can be fixed by 1 per cent. tannic acid and then washed with water without loss. After it has dried, the film thickness may be determined optically by interference colours.

MODERN POSITION ON SURFACE FILMS

The extraordinary interest which has been shown of recent years in the phenomena accompanying film formation on the surfaces of solutions is reflected in the great volume of literature regularly being published. The subject is in the main beyond the scope of this volume, but in view of the special character of the more recent work of the Cambridge school under Rideal, a very brief summary is necessary.[8]

Rideal in 1936 presented a succinct account of the developments to that date.[9] He pointed out that two methods were available to check the familiar concept of the oriented monolayer, such as the film of a long chain fatty acid floating on water ; the monomolecular layer has the hydrophilic groups immersed in the water with the hydrophobic chain extended above the surface. An optical method and an electrical method were outlined.

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[1] *J. phys.*, **3,** 450 (1904) ; *Compt. rend.*, **200,** 1560 (1935) ; **201,** 109 (1935).

[2] *Cold Spring Harbor Symposia on Quantitative Biology*, **6,** 171 (1938).

[3] *Trans. Faraday Soc.*, **33,** 1125 (1937).

[4] *Ibid.*, **33,** 1129 (1937).

[5] *J. Phys. Chem.*, **42,** 1089 (1938).

[6] Cf. Ställberg and Teorell, *Trans. Faraday Soc.*, **35,** 1413 (1939).

[7] See, for example, Bateman and Chambers, *J. Phys. Chem.*, **45,** 209 (1941).

[8] Useful summaries are given by : Rideal, *Chem. and Ind.*, **58,** 830 (1939) ; Germer, *Publications of the American Association for the Advancement of Science*, **7,** 47 (1939) ; Sobotka, *ibid.*, **7,** 54 (1939) ; Clowes, *ibid.*, **7,** 61 (1939) ; Bauer and Pollack, *J. Chem. Physics*, **3,** 401 (1935). See also Askew, *J. Chem. Soc.*, **1936,** 1585 ; Harkins, *Nature*, **148,** 743 (1941).

[9] *Proc. Roy. Soc.*, **A., 155,** 684 (1936). *Cf.* Harkins and Myers, *J. Am. Chem. Soc.*, **58,** 1817 (1936).

The latter method consists of examining the change in phase boundary potential at the interface due to the presence of the monolayer.[1] This change is caused by replacement of the free water surface by an array of polar groups, *e.g.*, hydrated COOH groups from the long chain fatty acid floating as a film and giving rise to a somewhat complex system of dipoles.

Adam's work [3] has shown that such films can exist in states analogous to matter in bulk phase [3]: solid, liquid condensed, liquid expanded, vaporous, and gaseous. In many instances, definite transition phenomena are observable and the states may be regarded as separate phases amenable to the application of the phase rule. Many films exhibit metastable states with a long time lag. Replacing one polar group with another, *e.g.*, COOH by OH, may alter expansion and contraction and even involve changes of phase; similarly with alteration of *p*H [4] or the presence of Ca ions underneath a fatty acid film.[5]

Rideal recognised another film structure, the *homalic*, in which state long, thread-like molecules are extended on the water surface, *e.g.*, monolayers of proteins, rubber, cellulose derivatives, phenol aldehyde condensation products and the polymers of ω-hydroxy acids and the drying oils. Relatively large areas of continuous sheets are possible from cross-bridged monolayers. Changes in phase boundary potential lead to definite evaluation of the apparent electric moment of the repeating unit in the macro-molecule, *e.g.*, CO-NH-CHR- in protein. "The properties of these macro-molecular monolayers are worth detailed examination as they are the precursors of natural membranes."

Extremely interesting is the formation of mixed films when an existing film is penetrated by material from the substrate.[6] Thus, beneath a film of an alcohol, a very little of a dilute solution of a long chain sulphonic acid is introduced and a loose complex obtains between the head groups. In time, the hydrocarbon chain of the sulphonic acid penetrates into the aqueous layer between the head groups of the film of alcohol, enters the middle water/oil phase of the triplex film and ascends into the top oil layer. The final and remarkably stable film consists of equal quantities of acid and alcohol. Two factors determine the penetration and stability of the resulting film: (1) the primary head group complex formation which initiates the process, (2) the van der Waals adhesion of the chains. Complexes of markedly specific character are often formed when ring systems such as cholesterol and saponin are employed in place of chain molecules.

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[1] Yamaguchi and Mizuno, *Bull. Chem. Soc. Japan*, **10**, 453 (1935); *J. Electrochem. Assoc. Japan*, **3**, 2 (1935); Chalmers and Pasquill, *Phil. Mag.*, **23**, 88 (1937); Bikerman, *Trans. Faraday Soc.*, **34**, 800 (1938).

[2] *Proc. Roy. Soc.*, **A., 155**, 690 (1936).

[3] Mitchell, *Trans. Faraday Soc.*, **31**, 980 (1935); Tamamushi, *Bull. Chem. Soc. Japan* **9**, 363; 475 (1934); Harkins and Boyd, *J. Phys. Chem.*, **45**, 20 (1941).

[4] Myers, *J. Am. Chem. Soc.*, **57**, 2734 (1935).

[5] Langmuir and Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936).

[6] Myers and Harkins, *J. Phys. Chem.*, **40**, 959 (1936); Fowkes, Myers and Harkins, *J. Am. Chem. Soc.*, **59**, 593 (1937).

Schulman [1] is an outstanding authority in this field. Mentioning that the measurement of phase boundary potentials and surface pressures at air/liquid boundaries have been employed to examine the interaction between large molecules, he points out that one can distinguish between the dipole interaction as characterised by adsorption and the adhesion between the hydrophobic groups characterised by penetration. The latter is accompanied by a large increase in surface pressure of the film-forming substance, well above the possible surface tension lowering of the aqueous solution by either of the components individually.

" Owing to the arrival of a new dipole in the surface layer, penetration is always accompanied by a change in the phase boundary potential, the extent depending on the nature of the penetrating dipole. The ultimate surface potential is identical with that caused by a mixed film containing equimolecular proportions of the two molecules at maximum compression. Anchoring of the dipoles of the two molecules by adsorption is evidently essential before the hydrophobic groups can associate. The rise in surface pressure is readily understood, if every film-forming dipole anchors a dipole from the solution, the two molecules then associating ; thus the surface concentration has doubled, which has the same effect on the surface pressure as compressing the film to half its original area."

Schulman also points out that a stable mixed film may result even when one of components is alone too soluble to exist as a coherent film. Again, where the interaction is weak, compression may drive one component out of a mixed film.

Very important for the subject of emulsions is the formation and character of films at liquid/liquid boundaries which will be discussed later (see p. 56). For further data on air/liquid surface films reference should be made to the advances from the laboratories of Gorter,[2] Harkins,[3] Langmuir [4] (particularly in connection with built-up films [5]), and others.[6]

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[1] Schulman and Hughes, *Biochem. J.*, **29,** 1236 ; 1243 (1935) ; Schulman and Rideal, *Proc. Roy. Soc.*, **B., 122,** 29 (1937) ; Marsden and Schulman, *Trans. Faraday Soc.*, **34,** 748 (1938) ; Schulman and Teorell, *ibid.*, **34,** 1337 (1938) ; Schulman and Stenhagen, *Proc. Roy. Soc.*, **B., 126,** 356 (1938) ; Schulman, *Ann. Repts., Chem. Soc.*, **36,** 94 (1940).

[2] Harkins, Carman and Ries, *J. Chem. Physics*, **3,** 692 (1935) ; *J. Am. Chem. Soc.*, **57,** 776 (1935) ; **58,** 1377 (1936) ; *J. Chem. Physics*, **4,** 228 (1936) ; Harkins and Anderson, *J. Am. Chem. Soc.*, **59,** 2189 (1937) ; Fourt and Harkins, *J. Phys. Chem.*, **42,** 897 (1938) ; Harkins, *Publications of the American Association for the Advancement of Science*, **7,** 19 (1939).

[3] Gorter, *J. Gen. Physiol.*, **18,** 421 (1935) ; Gorter and Seeder, *ibid.*, **18,** 427 (1935).

[4] Langmuir, Schaefer and Sobotka, *J. Am. Chem Soc.*, **59,** 1751 (1937) ; Langmuir and Schaefer, *ibid.*, **59,** 1762 (1937) ; **59,** 2400 (1937) ; Langmuir, *ibid.*, **60,** 1190 (1938) ; *Symposia on Quantitative Biology*, **6,** 171 (1938) ; *Publications of the American Association for the Advancement of Science*, **7,** 9 (1939) ; Langmuir and Schaefer, *J. Am. Chem. Soc.*, **60,** 1351 (1938) ; Schaefer, *J. Phys. Chem.*, **45,** 681 (1941) ; Adam, *Sci. Progress*, **33,** 690 (1939).

[5] Langmuir and Blodgett, *Kolloid-Z.*, **73,** 257 (1935) Blodgett, *J. Am. Chem. Soc.*, **57,** 1007 (1935) ; *Phys. Rev.*, **55,** 391 (1939). See also Porter and Wyman, *J. Am. Chem. Soc.*, **59,** 2746 (1937) ; **60,** 1083 (1938) ; Bernstein, *ibid.*, **60,** 1511 (1938) ; Stenhagen, *Trans. Faraday Soc.*, **34,** 1328 (1938).

[6] Porter, *J. Am. Chem. Soc.*, **59,** 1883 (1937) ; Washburn and Wakeman, *ibid.*, **60,** 1294 (1938) ; Neville and Hazlehurst, *J. Phys. Chem.*, **41,** 545 (1937) ; Ford, *ibid.*, **40,** 835 (1936) ; Ford and Wilson, *ibid.*, **42,** 1051 (1938) ; Achmatov, *Kolloid-Z.*, **77,** 20 (1936) ; Seastone, *J. Gen. Physiol.*, **21,** 621 (1938) ; Neurath, *J. Phys. Chem.*, **42,** 39 (1938) ; Alexander, *Trans. Faraday Soc.*, **37,** 426 (1941).

CHAPTER II

ADSORPTION AT LIQUID/LIQUID INTERFACES

WHEN two immiscible liquids are in contact, the boundary surface between them is referred to as the liquid/liquid interface, or the dineric interface. This is not an absolutely distinct line of demarcation, but rather a very attenuated layer of molecular dimensions, due to the interpenetration of both phases. The physical properties of this layer differ from those of the interior of the two contacting phases. In emulsions, irrespective of the phase-type, there exists a relatively great interfacial separating layer, the area of which increases very rapidly with increasing subdivision of the internal phase.

ANTONOW'S RULE

The surface tension at the boundary between two immiscible liquids is termed the interfacial tension. Since, however, the liquids are never absolutely immiscible, the intersolubility of the phases must always be taken into account. For two completely soluble liquids it is usually stated that the interfacial tension is zero. Woodman,[1] however, investigating the system : aqueous acetic acid/toluene at 25° C., believes that mere coincidence in the values of the surface tensions of the phases, with a zero interfacial tension, are alone insufficient to cause complete miscibility ; "the zero value of the interfacial tension must coincide, apparently, with a zero rate of alteration of tension with respect to concentration."

A rule due to Antonow [2] states that the interfacial tension of two liquids *in equilibrium* is related to the surface tension of each. Thus :—

$$\sigma_{ab} = \sigma_a - \sigma_b$$

where σ_{ab} = interfacial tension at the liquid/liquid boundary. σ_a and σ_b = surface tensions of liquids A and B respectively at the vapour/liquid boundary.

Investigations by Reynolds [3] and Pound [4] confirmed the rule. Later, Woodman [5] has confirmed it for the system : aqueous acetic acid/toluene, whilst Nellensteyn and Roodenburg [6] found it valid for the system : bitumen/water. Deviations are now well recognised and the rule has received considerable attention of late.

Fuchs [7] measured the contact angles of a varied series of 48 organic compounds on water, all the compounds possessing positive spreading coefficients. The measure of deviation from Antonow's rule is given by :

$$\Theta = \Delta / \sigma_{ab}$$

where $$\Delta = \sigma_{ab} + \sigma_b - \sigma_a$$

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[1] *J. Phys. Chem.*, **31,** 1743 (1927).

[2] *J. Russ. Phys. Chem. Soc.*, **39,** 342 (1907) ; *J. chim. phys.*, **5,** 372 (1907) ; *Kolloid-Z.*, **59,** 7 (1932) and **64,** 336 (1933) ; *Ann. Physik.*, **35,** 84 (1939) ; *J. Phys. Chem.*, **46,** 497 (1942). See also Loman and Zwikker, *Physica*, **1,** 1181 (1934).

[3] *J. Chem. Soc.*, **119,** 466 (1921).

[4] *J. Chem. Aoc.*, **123,** 578 (1923) ; *J Phys. Chem.*, **30,** 791 (1926).

[5] *Loc. cit.*

[6] *Kolloid-Z.*, **63,** 339 (1933).

[7] *Ibid.*, **52,** 262 (1930).

No simple relation was found between Θ and molecular structure, and Θ diminishes with temperature for all the substances investigated. Fuchs proved the validity of the rule and the reality of Neumann's triangle (see p. 41). The deviations as measured by Δ lie between 0 and σ_{ab} and are probably related to the extent of orientation of the molecules in the saturated adsorption layer, a conclusion shared by Taubmann.[1]

THE SPREADING OF ONE LIQUID ON ANOTHER

Of great importance in connection with the problem of Antonow's rule is the question of the spreading of one liquid on the surface of another. Harkins and his co-workers have given this matter detailed consideration, discussing the thermodynamics of the formation of a new surface when one liquid covers another. If a liquid *b* spreads over another liquid *a*, the surface *a* disappears, its place being taken by the surface *b*. At the same time the interface *ab* is formed. Thus S, the decrease in free energy accompanying spreading, will be

$$S = \sigma_a - \sigma_b - \sigma_{ab}$$

Now $$W_A = \sigma_a + \sigma_b - \sigma_{ab}$$

and $$W_C = 2\sigma_b$$

Hence $$S = W_A - W_C.$$

where W_A = the work of adhesion and W_C = the work of cohesion (see p. 49).

Harkins' rule, therefore, is "that spreading occurs if the adhesion between the two liquids is greater than the cohesion in the liquid which is in the position for spreading, while spreading does not occur if the cohesion is greater than the adhesion." That is, when

$W_A - W_C$ is + spreading occurs,
$W_A - W_C$ is − spreading does not occur.

It should be noted that if *a* spreads over *b*, the converse that *b* spreads over *a* is not necessarily true. In fact, nearly all organic liquids spread over water, but water spreads over very few organic liquids. As examples of organic liquids which spread on water (at 20° C.), the following may be cited from Harkins' table of 71 liquids[2] :—

Spreading Liquids

	$W_A - W_C$
Ethyl alcohol	50·4
Formic acid	35·5
Aniline	24·45
Chloroform	13·04
Phenetole	10·66
Trichlorethylene	5·09
Hexane	2·31
Octane	0·22

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[1] *Ibid.*, **62,** 76 (1933).

[2] Harkins and Feldman, *J. Am. Chem. Soc.*, **44,** 2670 (1922) Harkins in Alexander's ' Colloid Chemistry," Vol. I., p. 229.

NON-SPREADING LIQUIDS

	$W_A - W_C$
Ethylene dibromide	− 3·19
Carbon disulphide	− 6·94
Bromoform	− 9·58
Methylene iodide	− 26·46

The presence of a polar group is not essential to spreading, but a polar group increases W_A towards water much more than it does W_C; accordingly, the tendency is for $W_A - W_C$ to be positive. Conversely, non-spreading is, as a rule, due to a high value of W_C for the liquid tested.

A further development has been given by Harkins and Ginsberg,[1] employing the ζ-function of Gibbs, commonly designated as the Gibbs free energy F. They show that the spreading coefficient of a liquid *b* on *a* has two values, S and S′, the former being the initial coefficient of spreading before the surfaces become contaminated and the latter the final coefficient of spreading after the liquids, the films and the vapour attain equilibrium. Then :—

$$S_{\frac{b}{a}} = \sigma_a - \sigma_b - \sigma_{ab}$$

$$S'_{\frac{b}{a}} = (\sigma_a{}' - \sigma_b{}') - \sigma'_{ab}$$

They point out that for a valid Antonow rule, $S'_{\frac{b}{a}} = 0$, whilst for the spreading of *a* on *b*, $S'_{\frac{a}{b}} = 2\sigma_{ab}$.

It is emphasised regarding the latter equation that in the event of it being true, a remarkable restriction would be imposed on the phenomena of the spreading of liquids on liquids. Under conditions of equilibrium, lenses of liquid *b* could not exist on liquid *a*, although the converse would always happen. Such, however, is against experience.

Extensive quantitative data are given on the spreading of liquids. For example, with mutually saturated phases in equilibrium, the final spreading coefficient on water of C_6H_6, CS_2, methylene iodide and heptyl alcohol, which, according to Antonow's rule, should be zero, are : −1·49, −9·95, −24·19 and −5·90 respectively.

To employ the rule as a guide in predicting interfacial tensions, only those systems must be considered where one of the final coefficients of spreading is positive and " the prediction should not be expected to be at all exact, unless allowance is made for the negative value of S'_b, which is supposed by the rule to be equal to zero."

Carter and Jones [2] have confirmed the above conclusions. They observed two classes of systems which do not meet Antonow's rule : (1) the organic substance has a negative initial spreading coefficient on water, and (2) the organic substance has a high positive initial spreading coefficient, followed by the formation of an oriented adsorption film on the saturated aqueous phase.

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[1] *Colloid Symposium Monograph*, **6,** 23 (1928).

[2] *Trans. Faraday Soc.*, **30,** 1027 (1934). See also Dervichian, *Compt. rend.*, **201,** 333 (1935).

NEUMANN'S TRIANGLE

Another way of studying spreading phenomena is based on a consideration of forces instead of free energies and has been employed in an important paper by Coghill and Anderson.[1] This deals with the so-called Neumann's triangle.

Maxwell[2] pointed out that for three fluids to remain in contact equilibrium the sum of any two interfacial tensions must exceed the third. Neumann's rule in this respect is that the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to Aab, Bbc, Cca (see Fig. 5).

If this condition is not satisfied, the triangle is imaginary and the three fluids cannot rest in contact. The inequalities represented by the Neumann triangle serve as a basis for the prediction of spreading or non-spreading of one liquid or another. The behaviour of benzene and aqueous soap solution (sodium oleate) when superimposed one upon the other illustrates the use of the triangle. The table shown on the following page is given by Coghill and Anderson.

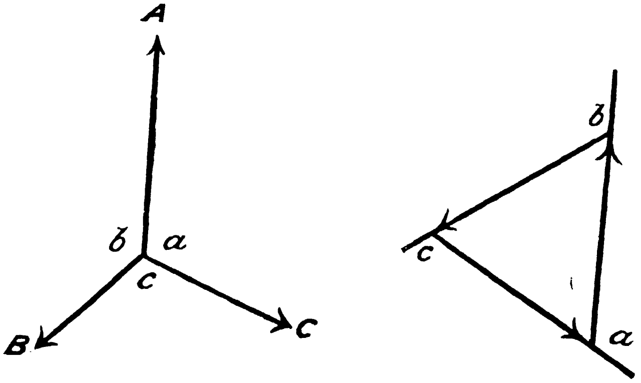

FIG. 5. The Neumann triangle.

The most recent work in this field is a very thorough study by Miller on the tension mechanisms responsible for lens formation, the lens formation of those liquids which form films on water surfaces being ascribed to a decrease in free energy ($-\Delta f_0$) which occurs through the orientation of the molecules in the film.[3]

One of three phenomena occurs spontaneously when a drop of a liquid (*b*) is placed on the surface of a substrate liquid (*a*) with which it has low mutual solubility : (1) the drop will spread over the water surface to form a continuous film of uniform depth ; (2) a small portion of the drop will form a continuous film, the bulk of the liquid remaining as a lens or a number of small lenses in equilibrium with the film ; (3) no film

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[1] U S. Bur. Mines, *Tech. Paper*, **262,** (1923), p. 54.

[2] *Encyclop. Brit.*, **5,** 263 (1910).

[3] *J. Phys. Chem.*, **45,** 1205 (1941). Cf. Bradley, *Trans. Faraday Soc.*, **36,** 999 (1940).

TABLE 5

BEHAVIOUR OF BENZENE AND AQUEOUS SOAP SOLUTION WHEN SUPERIMPOSED ONE UPON THE OTHER

No.	Strength of Solution (per cent.).	$T_{w,a}$ Soap Solution, Air (dynes per cm.).	$T_{o,a}$ Benzene, Air (dynes per cm.).	$T_{w,o}$ Soap Solution, Benzene (dynes per cm.).	Triangle of Forces.	Inequalities.	Behaviour of liquids.	
							Benzene superimposed.	Aqueous Solution superimposed.
1	0·0000	73	29	35	Imaginary	$T_{w,a} > T_{o,a} + T_{w,o}$..	Spreads.	Sinks.
2	0·0012	68	29	34·7	,,	$T_{w,a} > T_{o,a} + T_{w,o}$..	,,	,,
3	0·0025	63	29	34·5	Real	$T_{w,a} > T_{o,a}$; $T_{w,o} > T_{w,a} - T_{o,a}$.	Forms lens and floats.	Forms globule and floats.
4	0·0100	49	29	33	,,	$T_{w,a} > T_{o,a}$; $T_{w,o} > T_{w,a} - T_{o,a}$.	,,	,,
5	0·0300	34	29	23	,,	$T_{w,a} > T_{o,a}$; $T_{w,o} > T_{w,a} - T_{o,a}$.	,,	,,
6	0·0600	24	29	14	,,	$T_{o,a} > T_{w,a}$; $T_{w,o} > T_{w,a} - T_{w,a}$.	Forms flattened globule and floats.	,,
7	0·400	25	29	3	Imaginary	$T_{o,a} > T_{w,a} + T_{w,o}$..	Floats by buoyancy.	Spreads.

is formed, but the entire drop forms a lens which rests in the uncontaminated substrate surface.

Miller's paper must be referred to for its detailed discussion. Briefly, his theory requires that a liquid may form a lens by either phenomenon (2) or (3), provided its value of the sum of the surface tension of liquid *b* saturated with liquid *a* and the interfacial tension between these two liquids exceeds the effective tension of the substrate at equilibrium. Four tension mechanisms are described responsible for lens formation, supported by numerous data for lens angles and related tensions.

INTERFACIAL TENSION

An enormous literature pertains to interfacial tension measurements, all of which have interest in the study of emulsions. In biology there are such subjects as the relation of interfacial tension to bactericidal capacity,[1] the cytolysis of cells,[2] the behaviour of sera,[3] adsorption and narcotic action,[4] and the general question of cell membrane permeability.[5] The theory of wetting and of detergent action involves interfacial tension considerations.[6] In pure physical chemistry the subject has also much significance, as for example, in the theory of conjugated solutions.[7] Again, the interfacial tensions of water/*n*-butyl alcohol, water/isobutyl alcohol and glycerol/isobutyl alcohol have been determined by Silbereisen[8]

[1] Daniels and Lyons, *J. Phys. Chem.*, **35**, 2049 (1931).
[2] Page, Shonle and Clowes, *Protoplasma*, **19**, 213 (1933).
[3] Seelich, *Biochem. Z.*, **273**, 135 (1934).
[4] King *et al*, *J. Pharmacol.*, **40**, 275 (1930).
[5] Harvey and Shapiro, *J. Cellular Comp. Physiol.*, **5**, 255 (1934) ; Sivadjian, *J. pharm. chim.*, **17**, 457 (1933).
[6] Cf. Millard, *Ind. Eng. Chem.*, **15**, 810 (1923).
[7] Brun, *J. chim. phys.*, **29**, 184 (1932).
[8] *Z. physik. Chem.*, **143**, 157 (1929).

with a view to using such systems in determining the pore diameter of Bechold ultra-filters. Measurements of interfacial tension are, of course, fundamental in work on adsorption at the dineric interface.

Attention can be directed only to recent special aspects. Eversole and Dedrick [1] have dealt with the effect of dissolved electrolytes on the interfacial tension of water/'oil,' hoping to throw light on the boundary effects of strong electrolytes in solutions. A very accurate method was devised, based on the drop volume method. They observed that the interfacial tension of mineral oil/aqueous Na acetate solutions decreased hyperbolically as the salt solution increased in concentration from zero to 6 molal. In the case of Na formate, however, a distinct minimum was noted in the interfacial tension-concentration curve, and at high concentrations of Na formate the interfacial tension is *greater* than at zero concentration. Using toluene instead of mineral oil, with Na formate the curve was of the same type as with mineral oil, but Na acetate now showed an interfacial tension curve which passed through a very abrupt minimum.

The striking effect of high concentrations of salts in *raising* interfacial tension is new, except that Traxler and Pittman [2] found similar results with NaCl for the system: water/asphalt. The explanation advanced by Eversole and Dedrick is based on the theory of molecular orientation and the increased interionic attraction in the interface due to the dielectric constant gradient in the interfacial layer. "The exact location of the ions in the interfacial layer is determined as the resultant of three forces." The hydrocarbon end of the ion confers attraction to the oil phase, the COOH end is attracted by the water phase, whilst the electrostatic attraction of the Na ion which is hydrophilic also opposes the attraction to the oil phase. Thus a low concentration of the salt in aqueous solution means an increased attraction of the water phase for the carboxyl group, the equilibrium position being shifted toward the water side of the boundary. On the other hand, a large concentration of the salt decreases the attraction of the water phase for the carboxyl end of the ion, so that the equilibrium position shifts toward the oil side of the boundary.

Dedrick and Hanson [3] extended this investigation, accurately measuring the interfacial tension: water/benzene under the influence of Na acetate. They found that at very low concentrations, the interfacial tension of benzene/aqueous Na acetate showed a rapid decrease as the salt concentration was raised. After passing through a decided minimum at about 0·1 molal, a very abrupt increase in interfacial tension occurred with a small increase in the salt concentration. It then passed through a maximum, whose value exceeded the initial interfacial tension of water/benzene and then decreased hyperbolically as the solution approached saturation.

These authors accept the theory of Eversole and Dedrick that "any solute which is a strong electrolyte when dissolved in water will cause the initial lowering of interfacial tension and the subsequent increase at higher concentrations, provided one ion has a greater tendency than the other to leave the aqueous phase and go into the non-aqueous phase." It is believed that failure to observe this in other work is due to lack of careful measurements at sufficiently low concentrations. Following the initial decrease and the subsequent increase in interfacial tension, the effect of strong electrolytes at yet higher concentrations depends on a further factor which is the tendency of the electrolyte as a whole to pass through the dineric interface into the non-aqueous phase as doublets or undissociated molecules. When this tendency is appreciable, the secondary lowering of interfacial tension (I.T.) is observed; otherwise, the boundary tension will still rise as the salt concentration rises.

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[1] *J. Phys. Chem.*, **37**, 1205 (1933).

[2] *Ind. Eng. Chem.*, **24**, 1391 (1932).

[3] *J. Phys. Chem.*, **37**, 1215 (1933). See also Kidokoro, *Bull. Chem. Soc. Japan*, **7**, 280 (1932).

A very extensive literature has accumulated in connection with I.T determinations. Recent papers relate to an interface against mercury.[1] The practical application of I.T. data is reflected in studies with hydrocarbon oils,[2] the surface behaviour of dyes,[3] emulsifying agents such as sodium lauryl sulphate,[4] leather fatliquoring,[5] identification of sugars,[6] soap solutions,[7] and biological work such as the influence of capillary-active substances on the effect of vagus stimulation [8] and the influence of 1, 2, 5, 6-dibenzanthracene on the I.T. between oil and serum.[9]

Only some of the main trends of modern investigations can be dealt with in the space available, and they primarily concern the course of adsorption of ions, micelles and molecules at the oil/water interface.[10]

Hartley [11] has pointed out that any *amphipathic* substance, *i.e.*, one in which there is an asymmetrical distribution of water-attracting and indifferent groups in the molecule, will lower the interfacial tension between water and a non-polar liquid. The substance accumulates in the interface, the water retaining the attracting group and expelling the indifferent one into the " oil " phase.

He recalls that the I.T. values of non-polar oils against water are not permanently reduced by simple paraffin-chain salts, already existing as such in either phase, below 1 or 2 dynes/cm., and spontaneous emulsification does not occur. The first steep fall of the I.T. is arrested at the concentration where formation takes place of symmetrically hydrophilic micelles. This provides an alternative means for the water to expel the intruding paraffin-chains. It is competitive to the reduction of I.T. as occasioned by the driving of the chains into a pre-existing interface.

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[1] Glidden, *J. Am. Chem. Soc.*, **57,** 236 (1935); Culbertson and Hedman, *J. Phys. Chem.*, **41,** 485 (1937); **42,** 469 (1938); Hedman, *Research Studies State Coll. Wash.*, **6,** 102 (1938); Henry and Jackson, *Nature*, **142,** 616 (1938); Dunken, *Z. physik. Chem.*, **B., 47,** 195 (1940); Bon, *Compt. rend.*, **210,** (1940); Iyengar and Rao, *Proc. Indian Acad. Sci.*, **10, A.,** 20 (1939).

[2] Vellinger and Radulesco, *Compt. rend. congr. graissage*, **1931,** 360; *World Petroleum Congr., London*, **1933,** *Proc.* 2, 407; *Ann. combustibles liquides* **9,** 279 (1934); Trillat and Leprince-Ringuet, *Compt. rend.*, **196,** 1214 (1933).

[3] Vellinger and Delion, *ibid.*, **198,** 2084 (1934); Szasz, *J. Am. Chem. Soc.*, **62,** 3520 (1940).

[4] Nasini, Rossi and Santa, *Atti V. congr. nazl. chim. pura applicata, Rome*, **1935,** (I), 410 (1936).

[5] Balfe and Uryash, *J. Soc. Leather Trades Chem.*, **23,** 347 (1939).

[6] Stroganov, *Protoplasma*, **24,** 431 (1935).

[7] Kulkarni and Jatkar, *J. Indian Inst. Sci.*, **21, A.,** (Pt. 34), 395 (1938); Wajzer, *Compt. rend.*, **200,** 1148 (1935); Belcot, *Ber.*, **71, B.,** 967 (1938); Gay *et al.*, *J. chim. phys.*, **32,** 371 (1935); **33,** 831 (1936); **34,** 517 (1937); **37,** 19 (1940); **37,** 30 (1940).

[8] Tsobkallo, *Arch. sci. biol.* (*U.S.S.R.*), **46,** 88 (1937).

[9] Reuterwall, *Acta Radiol.* (*Stockholm*), **16,** 149 (1935).

[10] Cf. Addison, *Nature*, **144,** 783 (1939), on interfacial activity of short-chain isomers.

[11] *Trans. Faraday Soc.*, **37,** 130 (1941).

The argument then advanced to the aim of reducing the tendency to micelle formation by retaining the same amount of paraffin in an ion, but replacing the straight chain by two approximately equal branches. Although, at the same single ion concentration, the new compound will be less surface-active than the original, it will, if sufficiently soluble, continue to diminish the I.T.

Experimental verification of the idea was obtained by measuring the I.T. of suitable aqueous solutions against cyclohexane. Indeed, spontaneous emulsification was noted with compounds prepared by sulphonation of di-alkyl ethers of dihydric phenols.

Dealing with the topic " Breaks in Interfacial Tension Curves," Addison[1] presents graphs showing the interfacial tension between saturated aqueous solution of $PhCH_2OH$ and solutions (0–100 per cent.) in benzene of $PhCh_2OH$. At 6, 39 and 65 wt. per cent., $PhCH_2OH$ respectively, are exhibited a sharp break, a sharp minimum and a rounded maximum. It is concluded that these curves are indicative of an amphipathic adsorbate soluble in both phases, the two breaks representing the beginning and the end of interpenetration of two identical adsorbed films. In the case of $PhCH_2Cl$, soluble only in the benzene phase, no break is shown in the curve.

In a discussion of the properties of detergent solutions, Powney and Addison[2] dealt with the surface and interfacial tensions of aqueous solutions of alkyl sodium sulphates having chain lengths from 12 to 18 carbon atoms. Interfacial tensions were determined against xylene. Plotting interfacial tensions against concentration of aqueous solution resulted in curves which showed well-defined breaks at certain critical concentrations which are dependent upon temperature and chain length. Such breaks are interpreted as coinciding with a sharp transition in bulk solution from single ions to micelles and the results are discussed in the light of Murray's theory[3] that the single long-chain ions are mainly responsible for the surface activity. A further communication[4] concerns the effect of various added salts on the surface and interfacial tensions of these compounds and with the resulting modification of the critical concentration for micelles, wherein the valency of the added cation is the main factor.

A similar type of investigation by Matthews[5] studied the influence of several carbohydrates (sugars, pectins and gums) upon the interfacial tension at the boundary : water/cyclohexane. The shape of the capillary curve obtained when the lowering of the I.T. is plotted against the concentration of the aqueous solutions depends on the type of monomolecular surface film present at the interface and this in turn depends on the shape of the carbohydrates molecules constituting the film. Matthews concludes that whilst molecules of dextrose, lactose, sucrose and gum arabic form gaseous films over the main range of concentrations investigated, dextrin gives a non-condensed film at low concentrations and a condensed film above a critical concentration. Citrus and apple pectins give an intermediate type of film, glycogen a film approximating to a vaporous one and starch a non-determinable orientation.

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[1] *Nature*, **144**, 249 (1939).
[2] *Trans. Faraday Soc.*, **33**, 1243 (1937).
[3] *Ibid.*, **31**, 206 (1935).
[4] *Ibid.*, **33**, 1253 (1937).
[5] *Ibid.*, **35**, 1113 (1939).

Whilst it is generally conceded that simple salts raise the surface tension of water, the effect on I.T. was not clear until recently. Lewis[1] and Kidokoro[2] had observed opposite effects for the influence of salts on the I.T. of water against a saturated hydrocarbon and at the suggestion of Lewis, Evans[3] investigated the effect of uni-univalent electrolytes upon the I.T. between *n*-hexane and water.

With NaCl, KCl, RbCl, CsCl and KNO_3, over the concentration 0 to 0·70 moles/litre, the I.T. showed a progressive increase, whereas with LiCl and NaOH there was an initial fall followed by a rise. KCNS showed an initial rise and then a fall.

Guest and Lewis[4] followed up this work, investigating the effect of electrolytes upon the I.T. between water and dekalin (*trans*-decahydronaphthalene). The work was carried out at 25° C., using aqueous solutions of KCl, LiCl, $BaCl_2$, $LaCl_3$, $AlCl_3$, KI, KSCN, LiI and LiSCN.

The last four salts caused a lowering of the I.T. with increase in the concentration of the active individuals (iodide and thiocyanate ions) and no explanation is advanced for such specific capillary activity.

Out of the five chlorides examined, the lithium and lanthanum salts exhibited a minimum in I.T. in the dilute region followed by a rise beyond that given by water alone against dekalin. The existence of the minimum is accounted for on Doles theory (see p. 8), which, however, could not be applied to the results obtained with KCl and $BaCl_2$, which apparently do not exhibit a minimum.

From the many published results on the electrophoretic mobility of colloidal particles in aqueous media as influenced by the presence of electrolytes, a common type of curve relating mobility to salt concentration is that where the mobility shows an initial rise as the salt concentration is increased, passes through a maximum at a low concentration and thereafter decreases continuously or to a limiting mobility. Thus, Breese and Lewis[5] found that KCl, KI, and KSCN affected the electrophoretic mobility of tristearin at constant $p\text{H} = 4$ and obtained a " normal " type of curve with KCl which showed the initial rise to a maximum and then a fall to a limiting value. With the other two salts, however, the mobility first decreased as the salt concentration increased ; the mobility passed through a minimum at a concentration of about

[1] *Phil. Mag.*, **6**, 17 ; 466 (1909).
[2] *Bull. Chem. Soc. Japan*, **7**, 280 (1932).
[3] *Trans. Faraday Soc.*, **33**, 794 (1937).
[4] *Proc. Roy. Soc.*, **A.**, **170**, 501 (1939).
[5] *Trans. Faraday Soc.*, **34**, 1515 (1938).

0·02 N, and subsequently rose as the salt concentration was raised, the effect being more pronounced with KSCN.

The suggestion was made that this effect may be due to the primary adsorption of SCN and I ions at the interface, whereby the electrokinetic surface charge density was increased and so the electrophoretic mobility. That such an effect might be connected with the observed lowering of I.T. at an oil/water interface in the presence of iodides and thiocyanates led to an investigation by Dickinson.[1] Cetyl acetate was used and I.T. and mobilities determined. A general parallelism was noted between the data in the case of KI and KSCN. The electrophoretic mobilities and the I.T. values indicated that for the lower concentrations the iodide ion is adsorbed to a greater extent than the thiocyanate ion, this order being reversed as the salt concentration was increased.

On the assumption that the formation of interfacial films affected both electrophoretic mobility and the lowering of I.T., a qualitative agreement might be expected between the two sets of data. Powney and Wood,[2] however, record several instances where high mobilities due to surface-active ions were accompanied by little or no lowering of I.T. The outstanding anomaly in this connection was exhibited by dodecyl pyridinium iodide. "Whilst the mobility of Nujol in water is – 4·35 μ/sec./volt/cm. at 25°, the addition of only 0·000075 % $C_{12}H_{25} . C_5H_5N . I$ reduces the mobility to zero and on further increasing the concentration to 0·0004 % the mobility attains a maximum value of + 5·8. Lowering of interfacial tension, on the other hand, is quite appreciable at concentrations below 0·01 % and it is only when the critical concentration (approximately 0·4 %) is reached that the mobility and interfacial tension data show any correlation. The high positive mobility shown at extremely low concentrations can only be due to the dodecyl pyridinium cations and the question arises as to whether these long chains will be situated actually in the oil-water interface, a process which might be favoured by the strong electrostatic attraction, or be present as an atmosphere in proximity to the interface. If there is definite adsorption, then it is difficult to understand why there should be no measurable interfacial activity even at concentrations twenty times higher than those at which high positive mobilities are attained. On the other hand, if there is no adsorbed film in the normal sense of the term, it is difficult to reconcile the incomparably greater sensitivity of the mobility of Nujol towards $C_{12}H_{25}C_5H_5N . I$ than towards a simple uni-univalent electrolyte such as NaCl."

ORIENTATION AND ADSORPTION

For the study of emulsions the nature of the interface between two liquids is all important. Evidence was accumulated which supports the view that, when two pure liquids are in contact, their like parts orientate towards each other, the separating boundary surface then possessing a definite packing or structure of molecules. Thus, when an organic liquid and water make an interface, the organic radical turns towards the organic liquid, and the active or "polar" group towards the water. As an example we may consider a film of oleic acid [$CH_3 . (CH_2)_7 . CH : CH(CH_2)_7 . COOH$] spreading on water. The COOH groups "dissolve" in the water, *i.e.*, combine with the water by virtue of the secondary valences. The long hydrocarbon chain is orientated away from the water. The molecules of oleic acid arrange themselves in the surface of the water with their hydrocarbon chains packed in side by side and vertically above the COOH groups. A film of *monomolecular thickness* is thus produced. From such considerations it follows that the hydrocarbons, without active or polar groups which can combine with water, should not spread on a water surface, and experiment has definitely proved this with pure paraffin oil, which does not spread as a uniform film on water.[1]

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[1] *Ibid.*, **36**, 839 (1940).

[2] *Ibid.*, **37**, 152 (1941).

Having accepted the view that the liquid/liquid interface possesses a definite structure,[2] it is necessary to consider from the newer standpoint the interfacial changes occurring when an emulsifying agent becomes adsorbed at the surface.

Harkins has pointed out the general law that "at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt." The orientation of molecules in a liquid/liquid interface is such as to turn like groups towards like groups. The free energy decrease, when the surface of a given liquid comes into contact with the surface of a polar liquid like water, depends essentially upon the most active or polar group present in the molecule (*e.g.*, COOH), and also upon the size and shape of the molecule. Experiments show that the presence of such active or polar groups in a liquid is intimately connected with the solubility of the liquid in water, so that liquids possessing a low interfacial tension are more or less miscible. As Harkins puts it: "The solubility in water is related to the free energy decrease, which more or less perfectly measures the attraction of the active group for the water molecule."

Now the solubility of one liquid in another can be considered as the extreme case of continuously increasing the interfacial separating surface between the liquids[3]; there is then no interfacial tension. Emulsions being systems of two non-soluble liquids, it follows that the presence of active or polar radicles does not in such cases call into play sufficient residual valences. A third substance must be added, and for it to be effective it must be capable of assisting or making less abrupt the transition of one liquid to the adjacent phase. Thus, for two immiscible liquids an emulsifier will be adsorbed at their interface if this substance possesses molecular groups which will orientate some to one liquid and some to the other. The emulsifier must, in a sense, act as a bridge for the two dissimilar liquids. By being adsorbed at the interface, the tension there is diminished, and diminished interfacial tension permits increased subdivision of one of the liquids in the other.[1] Thus sodium oleate decreases the free energy between benzene and water, and promotes the emulsification of benzene in water. Which of the two liquids becomes dispersed as globules in the other liquid depends on the mode of orientation and the strength of the residual valences called into play when the emulsifying agent is adsorbed at the interface.

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[1] Hardy, *Proc. Roy. Soc.*, **86 A.**, 632 (1912); Edser, *Brit. Assoc. Colloid Repts.*, **4**, 301 (1922). See Barrillon and Woog, *Ann. combustibles liquides*, **13**, 223 (1938).

[2] Regarding the fact that such orientation is not static, cf. Adam, *Sci. Progress*, **21**, 438 (1927). An address on polar forces in liquids has been given by Hildebrand, *Science*, **80**, 125 (1934), and in his "Solubility of Non-Electrolytes" (New York: 1936) Chaps. IV. and V.

[3] *Vide* Mees, *Chem. Weekblad.*, **19**, 82 (1922).

To reiterate, the essential point regarding emulsifying agents in general is that they are orientated at the liquid/liquid interface, and orientated in such a way as to reduce the free surface energy to a minimum. The polar or active end of the emulsifier is orientated towards the more polar or active liquid, and the less polar end towards the less polar liquid. Thermodynamically this idea is thoroughly sound.

Harkins[2] has pointed out that the evidence for orientation at a surface is based on :

(*a*) the work of adhesion of organic liquids for water or mercury,
(*b*) the work of cohesion of organic liquids alone,
(*c*) a comparison of the energy of surface formation with that of vaporisation.

The adhesional work between organic liquids and water has been determined by Harkins, Clark and Roberts[3] who gave data for about seventy organic liquids. These data are fundamental for the study of adsorption and emulsions.

The breaking of a bar of cross-section of 1 cm.^{2} at a plane perpendicular to its length, leads to the formation of two new surfaces. Thus the work of cohesion is equal to twice the free surface energy per cm.^{2} or $W_C/2 = \sigma$, where σ is the surface tension. The adhesional work, W_A, is that which is done by the surfaces of two different liquids, each 1 cm.^{2} area, approaching to make an interface. Dupré's equation may be expressed

$$W_A = -\Delta\sigma = \sigma_1 + \sigma_2 - {}_{1\cdot 2},$$

where $-\Delta\sigma$ is the decrease in free energy when two surfaces meet. Harkins gives the total energy change when two surfaces meet as

$$E_A = -\Delta E_s = \sigma_1 + l_1 + \sigma_2 + l_2 - (\sigma_{1\cdot 2} + l_{1\cdot 2}),$$

where

E_A = total energy of adhesion.
E_s = total surface energy.
l = latent heat of the surface.

The adhesional work of an organic liquid for water is obviously related to the solubility of the liquid in water, and indicates the polar nature of molecular groupings in the molecule. As the symmetry of the molecule decreases, the difference $W_A - W_C$ increases, and this is strong evidence in favour of the orientation theory.

Extensive experimental data on the adhesional work between mercury and organic liquids has been presented by Harkins and Grafton[1] and Harkins and Ewing.[2] The whole subject is extensively treated in a further paper by Harkins and Cheng,[3] who give complete data on the surface and interfacial energy relations of twelve organic liquids.

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[1] Cf. Wilson and Barnard, *Ind. Eng. Chem.*, **14**, 690 (1922).
[2] Alexander's "Colloid Chemistry" (N.Y., 1926), Vol. I., p. 207.
[3] *J. Am. Chem. Soc.*, **42**, 700 (1920).

In illustration of the above considerations, we may consider water, octane and octyl alcohol.

The value of W_C for water, a highly polar compound, is 145·8 ergs, for octane 435 ergs, and for octyl alcohol 55·1 ergs. The work of adhesion W_A for water/octane is 43·8 ergs, but for water/octyl alcohol it is 91·8 ergs. Thus, the value W_C is high for polar compounds and low for slightly polar compounds. The value W_A increases with the polarity of both liquids, *e.g.*, octyl alcohol and water. Here, polar OH groups in the alcohol have to be pulled away from water, so that considerable work must be done against the orientation at this interface. Harkins[4] further shows that an even more convincing illustration is that the work required to pull an alcohol away from water is practically independent of the size of the molecule. Thus, methyl alcohol (1 C. atom), and octyl alcohol (8 C. atoms) give values of W_A with water of 95·5 ergs and 91·8 ergs respectively. Such a result points definitely to interface orientation.

"An increase in symmetry, without a change in the composition of the molecule, is found to increase the work of cohesion, and to decrease the work of adhesion towards water, which is exactly in accord with the hypothesis that the molecules in surfaces are oriented, since an increase of symmetry not only reduces the extent of orientation, but it also decreases the effect of such an orientation upon the energy values."

COAGULATION AT THE DINERIC INTERFACE

There is abundant evidence that adsorption at liquid/liquid interfaces occurs when aqueous solutions of colloidal materials are shaken with organic liquids.[5] Definite changes take place in dyestuffs at the interface.[6] Numerous studies have been made on the adsorption of metal and other hydrosols at dineric interfaces, with particular attention to gold hydrosol.[7] The formation of emulsions stabilised by red gold has been observed.

Preferential wetting undoubtedly underlies the phenomena, and the hydrosols may be considered as transition cases between colloidal solutions and suspensions of solid particles which have direct interest in the theory of emulsions.[8]

[1] *J. Am. Chem. Soc.*, **42,** 2534 (1920).

[2] *Ibid.*, **42,** 2539 (1920).

[3] *Ibid.*, **43,** 35 (1921).

[4] Bogue's "Colloidal Behaviour" (N.Y., 1924), Vol. I., p. 157.

[5] Recklinghausen, "Uber die Kinetik der Koagulation an Grenzflächen," Thesis: Berlin, 1931.

[6] Deutsch, *Ber.*, **60 B.,** 1036 (1927) and *Z. physik. Chem.*, **136,** 353 (1928); Kolthoff, *Kolloid-Z.*, **43,** 51 (1927); Thiel, *Z. Elektrochem.*, **35,** 266 (1929); Janeso, *Kolloidchem. Beihefte*, **32,** 143 (1930); Efimow and Rehbinder, *Biochem. Z.*, **211,** 154 (1929).

[7] Reinders, *Kolloid-Z.*, **13,** 235 (1913); Zsigmondy, *Z. anorg. Chem.*, **96,** 265 (1916) and *Z. Elektrochem.*, **22,** 102 (1916); Yanek, *Ann. école mines Oural*, **1,** 45 (1919); Lepeschkin, *Kolloid-Z.*, **39,** 46 (1926); Janek and Schmidt, *inid.*, **66,** 296 (1934); Freundlich and Loebmann, *Z. physik. Chem.*, **A., 139,** 368 (1928); Bolam and Crowe, *J. Phys. Chem.*, **35,** 1448 (1931); Brönsted and Warming, *Z. Physik. Chem.*, **Abt. A., 155,** 343 (1931).

[8] Van der Minne, *Chem. Weekblad.*, **27,** 651 (1930); Carrière, *ibid.*, **27,** 638 (1930).

INTERFACIAL ADSORBED FILMS

The Gibbs adsorption equation predicts concentration changes at interfaces (see p. 5) and such changes are fundamental in the study of emulsions. The concentration change may be of such a character as to lead to the presence of a distinct film at a suitable liquid/liquid interface and investigations have been conducted on this point for very many years.

The earlier work on the concentration of solutes at boundary surfaces was done in connection with foams, *i.e.*, at the liquid/air interface.[1] Ramsden [2] in 1894 had shown that agitation of various protein solutions caused separation of part of the dissolved protein as fibrous or membrano-fibrous solids ; egg albumin, for example, could be coagulated and totally removed from solution by sufficient agitation. Numerous solutions and suspensions were similarly made to yield solid free-surface coatings, which in some instances were not resoluble in the mother liquor. Ramsden showed that such spontaneous desolutions of previously dissolved matter at the free surface was due to the accumulation at the surface of the solute owing to its being adsorbed there because of the lowering effect on the surface tension. Agitation or shaking simply served to increase and expose the free surface.

Ramsden [3] then showed that in the case of several persistent emulsions, actual solid membrane separated out at the liquid/liquid interfaces, *e.g.*, between olive oil and saponin solutions. The membrane manifested itself in such phenomena as (1) the intense viscosity at the interface, (2) the deformed appearance of otherwise spherical dispersed globules, and (3) the appearance of semi-opaque membranes when the separating surfaces were appropriately deformed. It was concluded that "the persistence of many emulsions is determined largely, among other factors, by the presence of solid or highly viscous matter at the interfaces of the two liquids," and that "accumulation of solid matter at the interfaces of the above emulsion-pairs occurs because the surface energy is thereby diminished."

Similar enveloping films in emulsions have been visualised by Clowes [4] with olive oil emulsions, by Clark and Mann [5] with emulsions stabilised with egg albumin, and by Holmes and Cameron,[6] who dispersed water in a mixture of amylacetate and benzene, using cellulose nitrate as the emulsifying agent. Tough elastic films were clearly seen around the water globules. Nutting [7] has described the films which develop when many petroleums stand for a few weeks in contact with water. The films have great strength and, apparently, are in the nature of higher alcohols.

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[1] Hall, *Proc. Roy. Soc.* (*Dublin*), **9,** 56 (1899) ; Benson, *J. Phys. Chem.*, **7,** 532 (1903) ; Zawidzki, *Z. physik. Chem.*, **35,** 77 (1900) ; **42,** 612 (1903) ; Metcalfe, *ibid.*, **52,** 1 (1905) ; Rohde, *Drude's Ann.*, **19,** 935 (1906).

[2] *Arch. Anat. Physiol.*, **(1894),** 517 ; *Z. physik. Chem.*, **47,** 336 (1904) ; *Trans. Liverpool Biol. Soc.*, **33,** 3 (1919).

[3] *Proc. Roy. Soc.*, **A., 72.** 156 (1903).

[4] *J. Phys. Chem.*, **20,** 407 (1916).

[5] *J. Biol. Chem.*, **52,** 182 (1922).

[6] *J. Am. Chem. Soc.*, **44,** 66 (1922).

[7] *Ind. Eng. Chem.*, **17,** 1036 (1925).

The qualitative aspect of adsorbed films may be considered as well established (see p. 56). The quantitative aspect is not so satisfactory. Several investigators have endeavoured to prove the quantitative validity of the Gibbs equation and to explain the discrepancies always observed.

Lewis[1] investigated the system: hydrocarbon oil/aqueous solutions of sodium glycocholate, determining the mass of solute adsorbed per cm.^{2} of oil surface and the interfacial tension between the oil and the solution.

A serious discrepancy exists between the theoretical and experimental results, there being nearly eighty times more adsorption in practice than was calculated from theory. He also observed similar discrepancies in the quantitative adsorption of dyestuffs of the oil/water interface. In a later paper, Lewis[2] has collected his results in the following table :—

TABLE 6

ADSORPTION AT AN OIL/WATER INTERFACE

Substance.	Adsorption per cm.^{2} of the substance assumed to be in the form of undissociated salt or in chemically equivalent ionic proportions.	
	Found Value.	Calculated Value.
	grm.	grm.
Sodium glycocholate . .	5×10^{-6}	7×10^{-8}
Congo red	$3{\cdot}7 \times 10^{-6}$	$1{\cdot}1 \times 10^{-7}$
Methyl orange . . .	$5{\cdot}5 \times 10^{-6}$	$1{\cdot}2 \times 10^{-7}$
Sodium oleate . . .	10^{-6}	10^{-8}
Caustic soda . . .	$1{\cdot}5 \times 10^{-7}$	$7{\cdot}5 \times 10^{-9}$

The substances exhibiting wide variations from the values calculated from the Gibbs equation are known to yield colloidal solutions in water, especially when concentrated. The Gibbs equation only applies to true (molecular) solutions, since it is derived on the strict assumption that there is only one adsorbable component, which must form with the solvent *one phase* only. Lewis[3] suggested the now generally accepted view that the discrepancies are due to the fact that these colloidal substances form a gelantinous or semi-solid skin around the oil globules. In deriving his equation Gibbs not only assumed that the solute and solvent must form one phase, but also assumed that adsorption of solute would not cause any change in the energy of the molecules of the solvent in the surface layer; such energy changes, however, are known to take place. Another assumption was that the liquid in the surface layer has the same density as in the bulk of the solution. It is quite probable, however, that a change in density does occur, owing to the high concentration and compressibility of the liquid in the surface layer.[4]

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[1] *Phil. Mag.*, **15**, 499 (1908).

[2] *Ibid.*, **17**, 466 (1909); Dubrisay, *Kolloid-Z.*, **86**, 274 (1939), gives a table including these and other results by different investigators.

[3] *Vide* criticism by Ferguson, *Manchester Memoirs*, **65**, (iv), 13 (1921).

[4] Lewis, *Phil. Mag.*, **17**, 490 (1909).

More recent attempts to verify Gibbs equation have been concerned with the air/liquid surface. McBain and Davies[1] employed a simple air-bubble method to measure accurately the absolute adsorption at an air/liquid surface, avoiding the errors in the earlier experiments of Donnan and Barker.[2] The aqueous solutions investigated were : *p*-toluidine,[3] amyl alcohol and camphor. In each instance the quantity of solute adsorbed much exceeded that corresponding to a monomolecular film. The authors thereupon concluded "that for these solutions of ordinary non-electrolytes over a wide range of concentration of solutions the surface consists of a saturated monomolecular film of solute resting upon a comparatively thick layer of concentrated solution, gradually falling off with depth to the bulk concentration of the solution." Such an effect is ascribed to chains of contiguous oriented molecules which extend downwards into the solution from the outermost monomolecular film.

Owing to so remarkable a discrepancy between observed adsorption and the predictions of the usually stated Gibbs theorem, $\Gamma = -\frac{c}{\mathrm{RT}}.\frac{d\sigma}{dc}$, McBain and Davies re-examine the basis upon which the thermodynamical treatment of the subject rests. The assumptions usually made are that (1) only two components are present anywhere in the system, and that (2) the only free energy of a surface is its surface tension multiplied by its area. Simplification of Gibbs equation by substituting concentration for activity leads to abnormal results. Again, the lack of agreement between observed data and those deduced from the simplified equation arises from the type of solute investigated. Surface-active solutes are, as a rule, by no means ideal and frequently possess limited solubility, with corresponding deviation from the ideal partial vapour pressure. "It should be clearly understood that the potential or activity is that exhibited by the solute in the bulk of the solution and is not affected by whatever complications occur at the surface ; the whole behaviour at the surface is governed by the potential within the ordinary homogeneous solution, and the potential of each component in the surface must equal this, no matter how complicated the actual surface may be."

Thus, even if a crystalloidal solute be adsorbed in colloidal form, its amount would still be that predicted from the properties of the bulk of the solution ; in such a case, the ready exhibition of colloidality in the solute infers the possession of a potential or activity different from that of an ideal solution.

The authors emphasise that although it is fundamental, seldom or never have true, 2-component systems been investigated in this connection. They cite the foam from a neutral soap solution ; such foam contains acid soap and, therefore, the free alkali remaining in the solution introduces a new and important variable component. Further, the Gibbs equation excludes electrical effects, whereas all surfaces are electrified.[4]

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[1] *J. Am. Chem. Soc.*, **49**, 2230 (1927).

[2] *Proc. Roy. Soc.*, **A.**, **85**, 557 (1911).

[3] Cf. Taubmann, *Z. physik. Chem.*, **A.**, **161**, 129 (1932).

[4] Gans and Harkins do not agree this ; *Colloid Symposium Monograph*, **6**, 37 (1928).

Later, McBain and Du Bois[1] measured the adsorption at the surface of solutions of iso-amyl alcohol, acetic, butyric, caproic and nonylic acids, phenol, *p*-toluidine, resorcinol, thymol, camphor and sodium chloride. From 2 to 8 times as much of the solute is transferred by an air bubble passing through the solution as is predicted by the Gibbs equation and the amounts transferred are from 2 to 4 times that which can be acommodated in a monomolecular film of closely packed vertically oriented molecules.

Direct measurements by the bubble method of the adsorption of *p*-toluidine and of iso-amyl alcohol at the air/liquid interface have also been made by Gans and Harkins,[2] whose results are in partial agreement with those of McBain and Davies, being, however, in general, smaller. Apparently, the adsorption decreases as the adsorbing bubbles grow smaller.

To avoid possible errors due to the use of moving surfaces, McBain and Humphreys[3] measured absolute adsorption at *static* air/water interfaces by a microtome method. Under these conditions the observed values of Γ agree quite closely with those predicted by the Gibbs equation, although the previously mentioned bubble experiments with the same solutes gave high results. "The Gibbs equation would thus appear as a limiting law." These results were confirmed by an interferometer method which detects the change in concentration when the surface of a solution is destroyed or submerged with consequent re-solution of the adsorbed material in the bulk of solution.[4]

More recent investigations into adsorption at the liquid/liquid interface have been conducted by Gibby and co-workers.[5] Their first paper dealt with the adsorption of methylene-blue, methyl-orange, Congo-red and orange-II at benzene/water and chlorobenzene/water boundaries. Marked quantitative variations from the values predicted by the Gibbs equation were observed in all eight instances. Two distinct types of concentration/adsorption curve were noted, differing according to the adsorbate, but independent of the interface examined.

The first type was exhibited by methylene-blue and orange-II, where the curve (abscissæ = dye concentration ; ordinates = dye adsorbed per cm.^{2}) rises fairly steeply to a maximum adsorption and remains constant. The second type exhibited by Congo-red and methyl-orange showed an initial rise to a sharp maximum, to be followed by a fall towards or reaching zero adsorption. In this type the organic liquid influences the results.

A second paper[6] concerned the adsorption of five dyes at paraffin/water and air/water interfaces. No adsorption was detected at the latter interface. The discrepancies between the observed values and those calculated from the Gibbs equation were particularly marked in the case of Bordeaux extra.

A third paper by Gibby and Argument[7] dealt with a mercury/water interface, thus removing any suggestion that diffusion was an interfering factor. Congo-red, Bordeaux extra, indigo-carmine X, and Solway ultra-blue B were the dyes employed. In each case the adsorption passed through a maximum as the concentration increased and was always positive. Interfacial measurements were determined and the values of the adsorption calculated therefrom by means of the Gibbs equation were not in agreement with the measured values and in some instances were negative.

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[1] *J. Am. Chem. Soc.*, **51**, 3534 (1929).
[2] *J. Phys. Chem.*, **35**, 722 (1931).
[3] *Ibid.*, **36**, 300 (1932).
[4] McBain, Mills and Ford, *Trans. Faraday Soc.*, **36**, 930 (1940).
[5] Gibby and Addison, *J. Chem. Soc.*, **1936**, 119.
[6] *Ibid.*, **1936**, 1306.
[7] *J. Chem. Soc.*, **1940**, 596.

Gibby argues that the Gibbs equation, $\Gamma = -c\frac{d\sigma/dc}{RT}$, is meant only to apply to the adsorption of a single component from a solution in which its behaviour is ideal with reference to concentration and the interface should be free from disturbances of an electrical double layer.[1]

COMPARISON OF ADSORPTION AT INTERFACES

Although a few investigations have been reported wherein was noted a general tendency for similarity quantitatively in effecting lowering surface tension and interfacial tension when the same compounds were examined at the water/air and water-organic liquid interfaces, it has remained for Bartell and Davis[2] to compare the extent of adsorption of a chemical compound at various interfaces. The nature of the interface at which adsorption occurs is a major factor in determining the extent of adsorption at that interface.

The authors studied boundary tension lowering and adsorption at four different interfaces: water/air, water/*n*-heptane, water/benzene, and water/methyl *n*-amyl ketone. These three organic liquids have quite different interfacial tensions against water: 50·8, 34·2, and 12·4 dynes/cm. at 25° C. respectively. The solutes investigated were ethyl alcohol, *n*-propyl alcohol and *n*-butyl alcohol. Determinations were made of boundary tension at the four interfaces while maintaining the same chemical potential (= at the same aqueous phase concentration) of the solute under investigation. Then solutions containing different aqueous phase concentrations of the solute were prepared and boundary tension measurements at all the interfaces were carried out at these new chemical potentials of the solute. In this way the relative effects on the various boundary tensions of given variations in chemical potential were examined directly, and the inaccuracies of separate adsorption calculations were eliminated.

An equation was derived by means of which the *ratios* of the actual adsorptions of a given solute at various interfaces can be determined from boundary tension measurements, provided certain conditions are strictly maintained. The adsorption of butyric acid and of the four alcohols mentioned was measured at the interface: water/paraffin hydrocarbon and was in each case found to be approximately the same as the adsorption of the substance in question at the surface of its aqueous solution. However, each substance is less effective at the water/benzene interface. Hence arises the question as to what factor is predominant in causing a surface-active material to be adsorbed to varying extents at different interfaces.

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[1] Cf. Doss, *Kolloid-Z.*, **86**, 205 (1939); Dubrisay, *ibid.*, **86**, 273 (1939).

[2] *J. Phys. Chem.*, **45**, 1321 (1941).

The authors point out that the total amount of free surface energy at an interface cannot be this prime factor in determining the extent of adsorption of a solute at that interface. Instead it is the *maximum* free surface energy *available* at an interface that decides the extent of adsorption. Thus, they state:

"Cognizance must be taken of the fact that all 72 ergs/cm.^{2} of free surface energy at the water/air surface are not available for purposes of adsorption. After total displacement of the water surface by a surface consisting entirely of solute, a free surface energy of at least 22 ergs/cm.^{2} remains. Thus, at most, only 50 ergs/cm.^{2} are available for the adsorption of solute. At the water/paraffin hydrocarbon interface all, or nearly all, of the free interfacial energy may be available for adsorption, depending on whether or not sufficient concentrations of solute can cause the water/organic liquid interface to disappear. In the case of each of the five solutes investigated, the available free surface energies at the two interfaces (water/air and water/paraffin) are nearly equal, and it is not surprising that the adsorption at the two interfaces should be so nearly the same.

"The maximum free surface energy available at the water/benzene interface is some 16 ergs/cm.^{2} less than that available at the water/paraffin interface. On the basis of this consideration, less adsorption would be predicted between water and benzene than between water and paraffin. This prediction is substantiated by the experimental findings. The maximum free interfacial energy available at the water/methyl *n*-amyl ketone interface is relatively small. The experimental results show that adsorptions at this interface are considerably less than at the water-air boundary or at either of the other two water/organic liquid interfaces."

DEMONSTRATION OF FILM FORMATION

Over 100 years ago Ascherson [1] published a paper which has extraordinary interest and which anticipates modern views. Dealing with the physiological utility of fats and the problem of cell formation, Ascherson commmented: "I was surprised at the simplicity of a theory which sufficiently explains the formation of cells by the aid of two substances to be found everywhere, in conformity with physical laws, and at the same time ascribes to the fats an indispensable function well calculated to make their constant presence in the germs of organic beings intelligible. To confirm this theory by experiment I endeavoured to find some means of actually producing the assumed coagulation of the albumin, and, with a pleasure which will be readily understood, I made the important discovery: *that coagulation in form of a membrane occurs inevitably and instantaneously when albumin comes into contact with a liquid fat,* and that consequently an oil cannot be surrounded even for a moment by an albuminous liquid without a vesicular membrane or a cell forming round it. For the sake of brevity I shall call the property of forming membranes by contact *Hymenogony*, and the membranes thus formed *Haptogen* membranes."

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[1] Translated in Hatschek's "The Foundations of Colloid Chemistry" (London, 1925), p. 13.

He pointed out that "the simplest way of producing this interesting phenomenon is to place a drop of fresh white of egg and a drop of olive oil close to each other on a glass plate and to unite their edges . . . the consequence is the almost instantaneous formation of a delicate and elastic membrane,[1] which, by a kind of contraction, soon becomes wrinkled, sometimes in a very regular fashion." Fig. 6 illustrates this experiment, the photograph being made in the writer's laboratory by Mr. F. J. Morse.

Ascherson describes the irregular and strange shapes assumed by distorted oil drops in aqueous egg albumin solutions. He was induced to regard hymenogony "as a physical property, as a kind of capillary condensation which proceeds at the surface of heterogeneous liquids in contact," a view acutely anticipating modern opinion.

Biological implications of great importance accompany this oil/water "capillary condensation," and attention is directed to the remarkable papers by Haas [2] who injected oil and esters into the intercellular medium of the subcutaneous tissues of animals. For example, when acid-free cod-liver oil and oxygenated methyl esters of unsaturated acids of cod-liver oil were injected into guinea-pigs, distinct membranes formed at the interface site of injection.

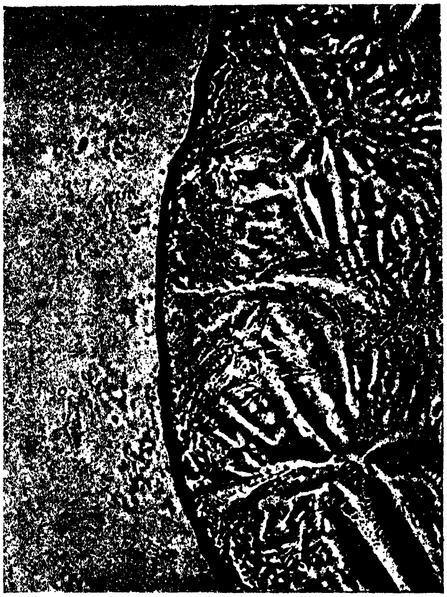

FIG. 6.—Interface: olive oil/aqueous egg albumin; × 162 (Morse).

The demonstration of the presence of interfacial membranes at oil/water interfaces is now thoroughly established [3] (Fig. 7).

In connection with interfacial films an important paper by Wilson and Fries [4] deserves attention.

These workers investigated film formation at air/liquid and oil/liquid interfaces using sodium stearate and oleate, Quillaja saponin, and commercial Turkey-red oil neutralised with NaOH. A torsion pendulum apparatus was employed to measure accurately the superficial viscosity of the films, different shearing stresses being obtained by allowing the amplitude of the swings to decrease gradually.

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[1] See important observations by Dean, *Trans. Faraday Soc.*, **36**, 170 (1940).

[2] *Arch. Path.*, **26**, 956; 1183; 1196 (1938); **27**, 15 (1939); **28**, 177 (1939). See Clayton, *Manufgr. Chemist* (Sept. 1941).

[3] For example, Wiegner, *Kolloid-Z.*, **15**, 105 (1914); Limburg, *Rec. trav. chim.*, **45**, 884 (1926); Seifriz, *J. Phys. Chem.*, **29**, 595; 600; 746 (1925); Winkelbech, *Z. angew. Chem.*, **18**, 1953 (1906); Friedman and Evans, *J. Am. Chem. Soc.*, **53**, 2898 (1931); Narwani, *Kolloid-Z.*, **70**, 297 (1935); Rehbinder and Wenström, *ibid.*, **53**, 157 (1930); Rochow and Mason, *Ind. Eng. Chem.*, **28**, 1296 (1936); Lepeschkin, *Kolloid-Z.*, **85**, 52 (1938); Don and Harrisoh, *ibid.*, **72**, 257 (1935); Devaux, *Compt. rend.*, **202**, 1597 (1936).

[4] *Colloid Symposium Monograph*, **1**, 145 (1923).

The results obtained with sodium stearate in aqueous solution showed: (i.) surface films even in the case of a 1 in 100,000 dilution of sodium stearate are plastic solids and not viscous liquids, (ii.) a time factor enters into film formation, (iii.) higher concentrations of the soap build up films more rapidly and eventually give stronger films.

Sodium oleate gave evidence of marked adsorption at the air/liquid interface, but only in the case of more concentrated solutions (greater than 1 : 5,000) was a plastic solid film formation made evident. Saponin showed a much better tendency to form films. The gradual growth of surface films was investigated by an ultra-microscope method, and the final thickness observed in the different solutions varied from 10 to 40 microns. The phenomenon is essentially a colloidal one.

FIG. 7. Films of emulsifying agent (Seifriz).

In the case of liquid/liquid interfaces the same film tendency was observed, but apparently the production of such films appears to require much higher concentrations than in the case of surface films. Photographs are given showing stable, distorted globules of oil, indicating the presence of plastic solid forces of considerable magnitude. Particularly was this the case with saponin as emulsifier.

Interesting work on the adsorbed film in emulsions of the water-in-oil type has been done by Holmes and Cameron,[1] who found that if several large drops of water are added to a solution of cellulose nitrate in a mixture of 1 part of amylacetate and 3 parts of benzene tough elastic films are seen to surround the water drops very rapidly. For quantitative results, seven emulsions were made by dispersing 40 c.c. glycerol in 25 c.c. of acetone solutions of cellulose nitrate, using a mechanical shaker holding seven bottles. The emulsions were then allowed to " cream " for eighteen hours, *i.e.*, the glycerol emulsion sinks and a clear upper layer of acetone cellulose nitrate solution appears. The cellulose nitrate content of 10 c.c. of this upper layer was determined and compared with the original strength of the solution, the difference in concentration corresponding to adsorption of the cellulose nitrate.

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[1] *J. Am. Chem. Soc.*, **44**, 66 (1922).

The values were plotted, the ordinates being adsorption of cellulose nitrate in the glycerol/acetone interface, and abscissæ the concentration in the clear layer above the emulsions. Instead of the usual curve characteristic of adsorption, an abnormal curve is given. At the start of the curve the adsorption isotherm is followed, but after this some radical change occurs. Holmes and Cameron believe that adsorption is here so rapid that precipitation or coagulation occurs at the glycerol-acetone interface.

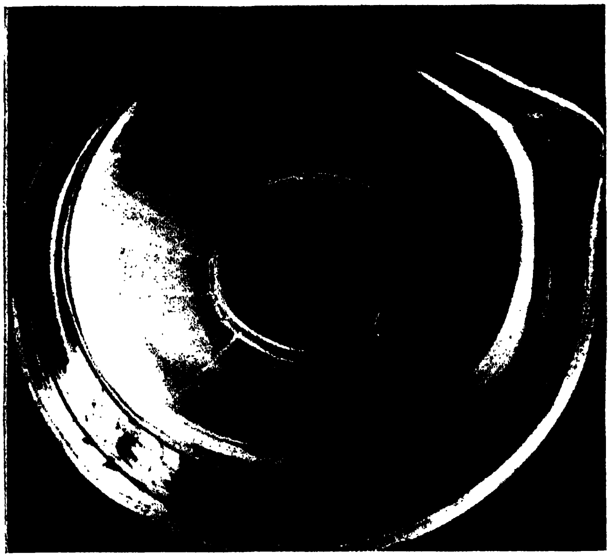

FIG. 8. Irish moss/mineral oil interface. Concentration 0·8 per cent.; age twelve days; temperature 26·67° C. (Serrallach and Jones).

Our knowledge of the formation of adsorbed interfacial films has been extended by the recent work of Serrallach and Jones,[1] who investigated the speed of formation of the films and their general characteristics. Their method was to place the aqueous solution in a beaker and carefully layer a volume of oil thereon. In some cases the film was easily visible; in others, the presence of the film was demonstrated by sinking a platinum ring to the interface so as to cause wrinkles in the film (see Fig. 8). The table shown on p. 60 is reproduced from the authors' report.

The authors point out that " the influence of the oils on the properties of the films was more definite than that of the emulsifiers. Cod-liver oil

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[1] *Ind. Eng. Chem.*, **23**, 1016 (1931). See review by Heymann, *Allgem. Oel. Fett.-Ztg.* **29**, 389 (1932).

TABLE 7

FORMATION AND PROPERTIES OF INTERFACIAL FILMS

General Properties of Films Formed at Room Temperature after 4 Weeks' Standing*

	OLIVE OIL.	CASTOR OIL.	COD LIVER OIL.	MINERAL OIL.
Sodium oleate	Opaque, granular, pulverulent, thick, weak	Transparent, very thin, weak	Opaque, granular, whitish, pulverulent, thick	Translucent, thin, very weak
Sodium glycocholate	Translucent, almost transparent, thin, weak	Transparent thin, weak	Opaque, granular, membranous, brittle, wrinkles	Thin, transparent
Triethanolamine	Transparent, weak, brittle	Transparent, weak, thin	Opaque, granular, weak, thick, brittle	No film
Saponin	Transparent, thin, weak, elastic	Transparent, thin, weak, plastic	Translucent, membranous, elastic, can be folded	Thin, transparent
Irish Moss	Opaque, strong, wrinkles	Transparent, very thin	Opaque, very thin, brittle, wrinkles	Translucent, membranous, thick, strong
Acacia	Transparent, thin, elastic, wrinkles	Transparent, very thin	Opaque, membranous, strong, brittle, wrinkles	Transparent, thin, wrinkles
Tragacanth	Transparent, wrinkles, brittle	Transparent, thin	Opaque, membranous, elastic, folds	Transparent, thin, weak, wrinkles
Gelatin	Translucent, thin, wrinkles	Transparent, thin	Opaque, membranous, brittle, wrinkles, folds easily	Transulcent, thin, weak, elastic

* Solutions contained no antiseptic.

Speed of Film Formation of Various Emulsifiers in Contact with Different Oils

(Observation time, 4 weeks)

	OLIVE OIL.	CASTOR OIL.	COD LIVER OIL.	MINERAL OIL.
Sodium oleate	Slow	Very slow	Very quick	Slow
Sodium glycocholate	Slow	Very slow	Very quick	Very slow
Triethanolamine	Very quick	Very slow	Very quick	No film after 4 weeks
Gelatin	Moderate	Slow	Quick	Very slow
Irish moss	Quick	Moderate	Quick	Very slow
Acacia	Quick	Slow	Quick	Quick
Saponin	Very quick	Very slow	Quick	Very slow
Tragacanth	Quick	Moderate	Quick	Very quick

NOMENCLATURE.

Very quick, within 24 hours
Quick, 1 to 2 days
Moderate, 2 to 8 days
Slow, 8 to 15 days
Very slow, over 15 days

formed an unmistakable film with all the emulsifiers. Its speed of formation was also remarkable, as shown in Table 7. With sodium oleate and triethanolamine the film was thick, granular, and opaque, but weak. With all the other emulsifiers cod-liver oil gave tough, opaque films. Some of them wrinkled when stretched with the wire loop. In some cases these films could be folded on themselves and then unfolded to their original condition. Olive oil comes next to cod-liver oil in the tendency to form films, but these films were in general weaker and thinner and more transparent than the films given by cod-liver oil. Castor oil has a lesser tendency to form films. The films were transparent and weak and did not wrinkle in any case. Mineral oil has the least tendency to form films of any of the oils studied. However, films were seen with the higher concentration of the emulsifiers, except triethanolamine, during the four weeks they were observed. Thin films which were tough enough to give wrinkles were obtained with tragacanth and acacia.

" At the interfaces where film formation took place, there is no doubt that the film was polymolecular, as it was readily visible and coherent. It therefore seems probable that in true emulsions the films formed may be thicker than monomolecular, provided the ratio of emulsifying agent to interfacial area is great enough."

STRENGTH OF INTERFACIAL FILMS

In a later communication,[1] the strength of emulsifier films at liquid/liquid interfaces was discussed. A modified Du Noüy interfacial tensiometer with platinum ring was used, and the force per centimetre was read directly from the vernier on the torsion head when the interfacial film was broken by the ring. Numerous systems were investigated at 25° C., and the authors present many graphs of their results.

In summing up they point out that each interface possesses its own specific and characteristic properties. However, they admit classification into four groups :—

(1) The film strength decreases throughout the period of the tests (eighteen days) : triethanolamine/mineral or olive oil, and sodium glycocholate/cod-liver oil.

(2) The film strength remains constant after a preliminary drop within the first few days : sodium oleate/mineral oil, castor oil ; triethanolamine/castor or cod-liver oil ; saponin/mineral or olive oil, and cod-liver oil with higher concentrations of saponin ; gum tragacanth/mineral oil ; gum acacia/mineral oil.

(3) The film strength increases slightly : saponin/castor oil ; gum tragacanth/olive, castor and cod-liver oil ; gum acacia/olive and castor oil ; Irish moss/castor oil ; sodium glycocholate/castor oil.

(4) The film strength increases considerably : sodium oleate/cod-liver oil ; saponin/cod-liver oil with low concentration of saponin ; gum acacia/cod-liver oil ; gelatin/mineral, olive, castor and cod-liver oil ; sodium glycocholate/mineral and olive oil.

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[1] *Ind. Eng. Chem.*, **25**, 816 (1933).

It is argued that it does not necessarily follow that the efficiency of an emulsifying agent depends primarily on the strength of the interfacial films. More important are the primary reduction in the interfacial tension and the rapidity with which the film forms. Later, its strength may be advantageous.

Finally, it should be noted that some of the films exhibited remarkable elongation before the ring broke through, stretching as much as 8 mm. being observed in some cases.

By a different technique, studying the duration of drops in interfaces, Rehbinder and Wenström[1] also investigated the formation and rigidity of interfacial films. In the case of mercury/aqueous saponin solution, the duration of a rent in the film gave data on rigidity. Distinction is made between " liquid " films (*e.g.*, isoamyl alcohol) and " solid " films (*e.g.*, saponin).

THE MUDD INTERFACE TECHNIQUE

A method having most interesting possibilities for investigating the properties of adsorbed films on emulsion globules has developed from a technique proposed in biological research by Mudd and Mudd.[2] In its original form a droplet of 0·85 per cent. NaCl containing the cells to be examined and a globule of oil are placed near to each other on a clean microscope slide. A large cover slip is placed on top of them. This results in both drops spreading into films which meet along a line across the slide. The oil tends to displace gradually the aqueous phase under the cover glass and the oil/water interface therefore moves slowly in the direction of the aqueous phase. By the use of a mechanical stage the slowly advancing interface is kept under observation, as it progressively overtakes the cells in the aqueous fluid. The information thus obtained relates to the wetting of the cells by both phases at the oil/water boundary; further, under certain conditions the cells are subjected to compressing or to stretching forces at the interface, and information is yielded regarding their plasticity and fluidity.

Nugent's modification,[3] using an oil and a drop of an emulsion, enables the experimental differentiation between two important protective properties of protein films : (1) their resistance to disruption under the action of interfacial and mechanical forces, and (2) their state of hydration *per se*. Thus, it has been found possible to demonstrate that the surface hydration of protective films of gelatin on olive oil globules varies in the same general manner with *p*H value over the range studied as does the hydration of gelatin particles in solution.

Fig 9, reproduced from Nugent's paper, illustrates the general types of behaviour observed in the study of oil droplets with protective protein films. The oil used is either pure medicinal paraffin oil or pure triolein.

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[1] *Kolloid-Z.*, **53**, 145 (1930). By means of a rotating disc method, Pokhil, *J. Phys. Chem.* (*U.S.S.R.*), **13**, 301 (1939), determined the strength of myristic and palmitic acid films at the water/benzene and air/water boundaries and found them similar.

[2] *J. Gen. Physiol.*, **14**, 733 (1930—31). See Watzadse, *Arch. ges. Physiol.* (*Pfluger's*), **222**, 640 (1929).

[3] *J. Phys. Chem.*, **36**, 449 (1932).

The oil has a specific effect, as is commonly recognised to-day in all emulsion studies.

The vertical lines in Fig. 9 represent successive positions of the advancing interface, and the small circles show the oil globule originally contained in the droplet of emulsion under investigation. By using very diluted emulsions attention is confined to single oil globules and a crowded interface is avoided. Nugent examined droplets of oil from 8 to 14μ in diameter and the speeds of interfacial advance varied from 3 to 8μ per second.

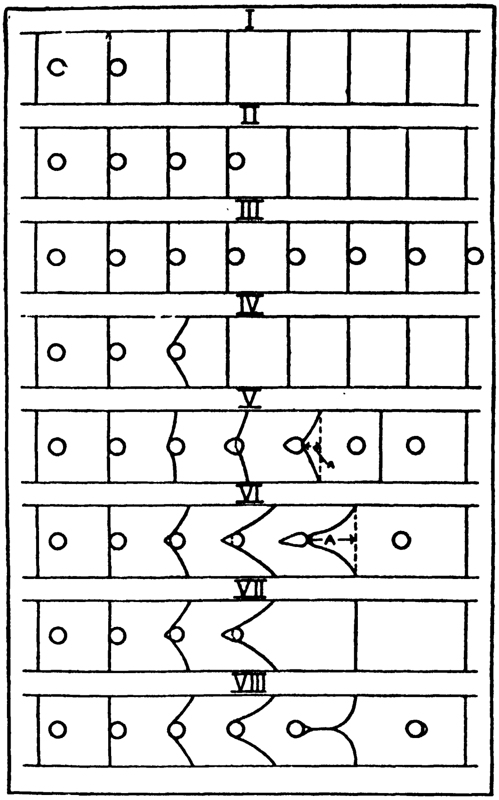

Fig. 9. Mudd interface technique (Nugent).

The first and second vertical columns depict the advancing interface in relation to an oil globule and the moment of contact respectively. The horizontal series depict the different behaviours observed. Thus :—

Case 1. Contacting with the interface causes the film (if any) protecting the oil globule to undergo immediate or very early disruption, the oil then dissolving in the oil of the advancing film, "exploding," as Nugent states. Unprotected oil globules show this phenomenon, as do globules enveloped with poor protecting material. It is argued that in the latter instance the emulsion film is practically immediately disrupted by the interfacial forces, indicating low film resistance and comparatively low film hydration.

Case 2. Somewhat greater resistance of the film to disruption or enhanced film hydration, or both, serves to prevent early explosion of the globule, *i.e.*, gives better protection against the disruptive action of the interfacial forces.

Case 3. This is the extreme of Case 2, the droplets being pushed before the advancing interface. The maximum protective effect of the adsorbed emulsion film is related to strong film resistance, to considerable film hydration, or to both.

Case 4. Here the globule is more or less firmly attached to the glass surface. After making contact with the droplet the interface suffers slight retardation. However, low film strength leads to ultimate explosion under the influence of interfacial forces or mechanical stresses.

Case 5. Again the globule is attached to the glass surface. The interface flows readily over the globule *which remains intact in the oil phase.* In this process the interface suffers only slight local retardation. The adsorbed film is apparently of considerable strength and of low hydration, as evidenced by the ease with which the oil phase wets it.

Case 6. The local retardation of the interface may be greater, indicating increasing hydration of the emulsion film material. By means of a micrometer ocular it is possible to measure the retardation of the interface at the moment of actual breaking away, leaving the oil globule intact in the oil phase. The distance is shown as " A " in Fig. 9. (Note that an oil-in-oil emulsion results.)

Case 7. This resembles Case 6, but the lesser resistance of the film to stretching permits ultimate explosion.

Case 8. Film hydration is here so marked that the advancing oil phase cannot flow *over* the globule but only *around* it, to unite again on the far side. The droplet now resides in the oil phase still surrounded by aqueous solution. The indication is of the greatest observable type of hydration and possibly of marked resistance to disruption under the action of the interfacial forces.

The behaviour of a film-enveloped oil globule at an oil/water boundary, insofar as it tends to show preferential progression into one of the contacting liquids, may be explained on the basis of wetting, *i.e.*, on the prevailing interfacial tensions. The argument in this respect is the same as for a solid particle in such an interface (see p. 217). Nugent's paper should be consulted for details of his various important experiments, including the interfacial behaviour at different *p*H values of butterfat globules from cream and the relation thereto towards churning.

A more recent application of the technique has been made by Moyer [1] to investigate the surface composition of latex particles from eighteen species of laticiferous plants.

MOLECULAR THICKNESS OF THE ADSORBED FILM

Considerable discrepancies have been reported concerning the question as to whether the adsorbed soap film at the dineric interface is monomolecular or polymolecular. Monomolecular films were deduced by Griffin [2] and by van der Meulen and Riemann.[3] The investigations of Harkins and Beeman [4] and Harkins and Fischer [5] also supported the idea of monomolecular films.

Mathews and Stamm[6] give data for the interfacial tension of dimethylaniline-heptane/water and dimethylaniline-benzene/water. They find that adsorption is one molecule thick up to concentrations where a complete surface layer is formed ; thereafter, the thickness begins to increase. The complete surface layer is formed only at high concentrations, probably because of polarity.

Studying the adsorption of butyric acid between water and hexane, Harkins and McLaughlin [7] found that the number of molecules in a monomolecular film at the interface is $2{\cdot}78 \times 10^{14}$ per cm.^{2}, corresponding to an area of 32 sq. Å per molecule, *i.e.*, the value found for this acid between benzene and water and water vapour. The film is tightly packed and " it seems evident that the number of molecules per unit area depends upon the dimensions of the molecules and their orientation."

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[1] *Am. J. Botany*, **22,** 609 (1935). The method has been employed in bacteriological research by Mellon, *Proc. Soc. Exptl. Biol. Med.*, **23,** 716 (1926). Harvey and Schoepfle, *J. Cellular Comp. Physiol.*, **13,** 383 (1939), describe a related technique involving the centrifuge.

[2] *J. Am. Chem. Soc.*, **45,** 1648 (1923).

[3] *Ibid.*, **46,** 876 (1924).

[4] *Ibid.*, **51,** 1674 (1929).

[5] *J. Phys. Chem.*, **36,** 98 (1932).

[6] *J. Am. Chem. Soc.*, **46,** 1071, 2880 (1924). See Sen, *Phil. Mag.*, **3,** 925 (1927).

[7] *Ibid.*, **47,** 1610 (1925).

Nonaka [1] studied the adsorption of soap at a benzene or toluene and aqueous soap solution interface and found that the adsorption of soap exceeded that calculated on the basis of the theory of the monomolecular layer. His idea is that of a *monomicellar* layer consisting of the neutral soap, while the free fatty acids are dissolved in the adsorbents.

Seymour, Taratar and Wright [2] have very carefully determined the adsorption of Na oleate at the benzene/soap solution interface in order to clear up the discrepancies. The technique employed was modified from that of McBain and his co-workers (see p. 53). "The results obtained were rather striking. In no case did the adsorption, as calculated from the gain in oleic acid, approach a monomolecular film. In fact, with one exception, the gain was more than twenty times that sufficient to form a film one molecule deep. The adsorption calculated from the gain in sodium was much less. Though we find no adsorption so small as a monomolecular layer, three runs gave values less than sufficient for a dimolecular film, and in only four runs were the gains greater than five times that for a single layer of molecules."

The authors draw attention to the work of others on the structure of soaps in solutions, which indicate the probable presence of large molecular aggregates in Na oleate solutions. It is to be expected that such aggregates would undergo adsorption at the benzene/water interface, in accordance with the results just mentioned.

As regards films in general it is to be expected that progressive, even if diminished, adsorption will proceed with time. This notion has been advanced by McBain.[3]

RECENT STUDIES ON INTERFACIAL FILMS

The experimental visualisation of interfacial films has now been replaced by laboratory measurements on them, usually applying technique adapted from the now well-established procedure on air/liquid films with a Langmuir balance.

The approach seems to have come from biological considerations. Danielli [4] took as the starting point the fact that the interfacial tension at the oil/water interface for oil droplets in mackerel eggs was less than 1 dyne/cm., due to an adsorbed layer of protein. He therefore investigated films of ovalbumin, pepsin, trypsin, hæmoglobin, serum globulins, and sturin at various oil/water interfaces.

Two methods were employed: (1) using a modified Adam-Langmuir trough, films of protein being spread at the dineric interface and then compressed in the two dimensions of the surface ; (2) using a du Noüy interfacial tensimeter to measure the tension at the interface.

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[1] *J. Soc. Chem. Ind. Japan*, **31**, 297 (1928).

[2] *J. Phys. Chem.*, **38**, 839 (1934).

[3] *J. Am. Chem. Soc.*, **49**, 2231 (1927). See also Harkins and Gans, *Colloid Symposium Monograph*, **6**, 36 (1928); Freundlich, *Ergebnisse exakt. Naturw.*, **12**, 82 (1933); Fuchs, *Z. physik. Chem.*, **B.**, **21**, 235 (1933); Guastalla, *Compt. rend.*, **196**, 1376 (1933) Damköhler, *Z. physik. Chem.*, **A.**, **169**, 120 (1934).

[4] Danielli and Harvey, *J. Cell. Comp. Physiol.*, **5**, 483 (1935); Harvey and Danielli, *Biol. Revs.*, **13**, 319 (1938); Askew and Danielli, *Proc. Roy. Soc.*, **A.**, **155**, 695 (1936); Danielli, *Cold Spring Harbor Symposia on Quantitative Biology*, **6**, 190 (1938). See as related papers, Danielli and Davson, *J. Cell. Comp. Physiol.*, **5**, 495 (1935); Danielli, *ibid.*, **7**, 393 (1936); *Trans. Faraday Soc.*, **37**, 121 (1941).

It was noted that at a brombenzene/water boundary there was a rapid spread of ovalbumin, only a few seconds sufficing for the initially spherical molecule to furnish a flat sheet or chain form, occupying an enormous area. The interfacial activity of the proteins at such an interface is extraordinarily high. Even at a dilution of one part by weight in one million of water a complete layer of protein forms at an interface in a few minutes. " Not only is the shape of the protein molecule changed by spreading, but also its solubility. If a thin film of protein is spread at an interface between oil and water, in the absence of protein in the bulk phases, the film will remain intact for hours, even under considerable compression, although the original native protein may have been very soluble indeed in the water. It would appear therefore that the changes in the molecule due to adsorption are so great that the adsorbed molecules must be regarded as a different molecular species from the molecules in the bulk phase."

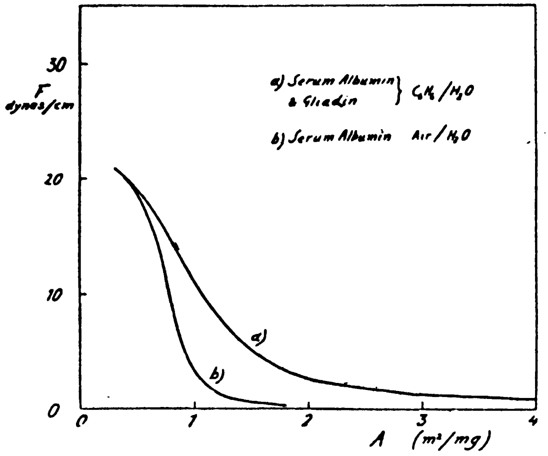

FIG. 10. *F*—*A* for serum albumin and gliadin at benzene/tap-water interface.
F—*A* for serum albumin at air/water interface (ring method).
Aqueous substrate *p*H 7·4 (universal buffer) + M/10 NaCl.

Alexander and Teorell[1] improved the technique for studying films at the dineric interface, employing the ring method as modified by Harkins and Jordan.[2] To obtain accuracy, the area was maintained constant and the interfacial concentration was increased by repeated injections of the spreading material into the interface. Force-area curves were determined for two proteins, gliadin and serum albumin, lysolecithin and sodium cetyl sulphate at the benzene/water interface.

At low pressures all films examined proved to be very much more expanded than at the air/water interface but at high pressures approximate to the air/water interface values. Fig. 10 is reproduced from the authors' paper.

Dealing with the equation of state at the benzene/water interface the authors write :

" According to the theory of expanded films developed by Langmuir[3] the equation of state of such films is given by the relation $(F—F_0)(A—A_0) = kT$. Here F_0 represents the negative spreading force of the hydrocarbon chains and A_0 is an empirical constant introduced to allow for the area occupied by the head-group. At the oil/water interface the F_0 term should accordingly be eliminated, whereas A_0 should remain unaffected. In order to test this the F—A curves of lecithin, lysolecithin and sodium cetyl sulphate were examined, by the method of displacement of co-ordinates, to see if they fitted a hyperbolic equation of the type $(F-F_0)(A-A_0) = C$. Up to about 15 dynes this relation was obeyed quite accurately, the values of F_0, A_0 and C being given in Table 8. For comparison purposes corresponding values obtained at the air/water interface are given in the same table.

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[1] *Trans. Faraday Soc.*, **35**, 727 (1939).
[2] *J. Am. Chem. Soc.*, **52**, 1751 (1930).
[3] *J. Chem. Phys.*, **1**, 756 (1933).

TABLE 8

	Benzene/Water Interface.			Air/Water Interface.		
	$-F_0$(dynes/cm.).	A_0(A²).	*C.*	$-F^0$(dynes/cm.).	A_0(A²).	*C.*
Lysolecithin . .	0·05	40·4	575	12·8	42·8	686
Lecithin . . .	0·36	58	737	8·7	51·2	728
Sodium cetyl sulphate	0·15	13·9	729	—	—	—

In agreement with Langmuir's theory the F_0 term, which at the air/water interface usually lies between 10–13 dynes, has been practically eliminated. Also the A_0 term is not appreciably affected by the change, and for sodium cetyl sulphate, which cannot be examined at the air/water interface, is of the usual order (14–19 A^2) as found for simple compounds at this interface.[1] The much higher values for lecithin and lysolecithin must be related to their large complex head-groups."

Alexander[2] has summarised the various methods for investigating insoluble monolayers at the oil/water interface, listing interfacial tension, viscosity and boundary potential changes.

In collaboration with Teorell and Åborg[3] Alexander has dealt with a specific effect of calcium ions on kephalin monolayers at benzene/water interface. The choice of kephalin arose from its position as an important member of the phosphatide group of cell lipoids and its bearing thereon in connection with the peculiar permeability displayed by living cells.

The experimental results obtained showed that although surface films of kephalin at the air/water interface are little affected by the nature of the ions present in the substrate, there is a marked and, apparently, specific effect at the benzene/water interface brought about by calcium ions. This is attributed to an "anchoring" of the kephalin molecules to the interface by the calcium ions, whereby the phosphatide material is prevented from dissolving in the benzene phase. Na, K and Mg ions did not show this effect. The explanation of the specific effect of Ca ions is given as the formation of a salt, insoluble in both phases, calcium uniting with the phosphoric acid groups of two molecules of kephalin, stabilisation in the interface arising from the dual causes of decreased solubility and doubling of the size of the molecule.

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[1] Marsden and Rideal, *J. Chem. Soc.*, **1938**, 1163.

[2] *Trans. Faraday Soc.*, 37, 117 (1941).

[3] *Ibid.*, 35, 1200 (1939). Cf. Danielli, *Proc. Roy. Soc.*, B., 122, 155 (1937).

Interfacial tension measurements demonstrate that a time effect exists, possibly beyond 24 hours. The unfolding of a globular protein adsorbed at an air/water surface may or may not proceed quickly to lead to a layer one polypeptide chain thick. That a similar behaviour may occur at an oil/water interface appeared probable and was investigated by Askew and Danielli.[1]

The surface balance was adapted for use at the interface between aqueous solutions and brombenzene. Surface pressure measurements were made on ovalbumin, alginic acid, trimethyl cellulose, α-aminopalmitic acid and *n*-eicosoic amide. It was found that these substances occupied larger areas per molecule than would be expected at the air/water interface, due to the brombenzene breaking down adhesions between non-polar parts of the molecules, " literally dissolving the CH_2 chains which, at the air/water interface, tend to hold adjacent molecules together."

At a given pressure ovalbumin films were less elastic than at the air/water surface, but the rate of unfolding was more rapid at the oil/water interface where all hydrocarbon adhesions will be " dissolved." [2]

INTERFACIAL TENSION AND EMULSIFICATION

A most important paper has been published by Harkins and Zollmann.[3] Data are given for the interfacial tension at the interface benzene/aqueous solutions of sodium oleate, with or without various solutes. Some extraordinarily low interfacial tension values were measured. Thus, the interfacial tension of the benzene/water interface is 35·0 dynes/cm. If now the aqueous phase contains NaCl and NaOH, each at 0·1N concentration, and the benzene phase contains oleic acid (0·1N), the interfacial tension is reduced to 0·04 dyne/cm., *i.e.*, about a thousandth of the former value. Reduction of the interfacial tension to below 10 dynes/cm. permits easy emulsification of the benzene, whilst spontaneous emulsification follows reduction of the tension to below 1 dyne/cm. Such emulsions remain stable for years.

Very low interfacial tension values are observable in biological systems. Thus, Danielli and Harvey [4] extracted the oil from mackerel eggs and measured the interfacial tension against sea water (7 dynes/cm.) and egg extract (0·8 dynes/cm.). Harvey and Shapiro [5] calculated the interfacial tension at mackerel egg oil/protoplasm to be 0·5 dynes/cm.

SPONTANEOUS EMULSIFICATION

Since the observation by Gad[6] in 1878 that spontaneous emulsification is possible in certain liquid/liquid systems (in his case, oil + fatty acid gently shed on to an aqueous solution of alkali), various investigators have reported similarly. The most recent is the finding by Schulman and Cockbain[1] that if an aqueous solution of sodium cetyl sulphate is poured into a solution of cholesterol in nujol, extensive emulsification occurs without any further shaking.

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[1] *Ibid.*, **36**, 785 (1940).

[2] Askew, *Proc. Roy. Soc.*, **A.**, **155**, 695 (1936).

[3] *J. Am. Chem. Soc.*, **48**, 69 (1926). See also Seelich, *Kolloid-Z.*, **85**, 268 (1938) on " Cation Effects at Surface Boundaries of Acid Character," especially Fig. 2 on p. 270.

[4] *J. Cellular Comp. Physiol.*, **5**, 483 (1935).

[5] *Ibid.*, **5**, 255 (1934). Harvey, *Trans. Faraday Soc.*, **33**, 943 (1937).

[6] *Arch. Anat. Physiol.*, **1878**, 181.

Very low interfacial tension between the two phases is the fundamental characteristic in this phenomenon. McBain and Woo[2] have described and photographed some beautiful results in this field (see Fig. 11) and conclude that the phenomenon of spontaneous emulsification in the absence of all external mechanical stirring is partly due to local movements resulting from lowered interfacial tension, but an important factor is the collision of molecules in diffusing columns driving other molecules with them.

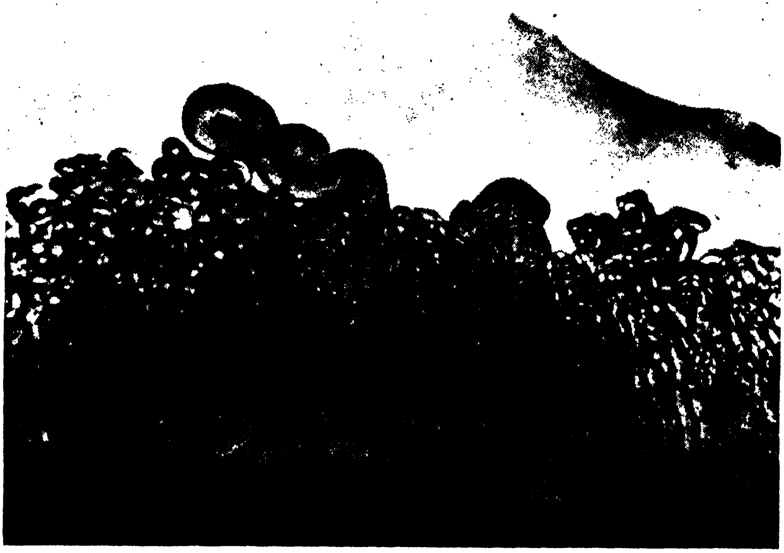

FIG. 11. A drop of "diglycol laurate" placed on a lens of water and spreading horizontally to give myelin forms.

They state that spontaneous emulsification was observed with diglycol laurate placed on water, and with nujol solutions of lauric acid (5 and 10 per cent.), palmitic acid (1 per cent.), montan wax (5 per cent.) and, *inter alia*, trimethyl dodecyl ammonium bromide (1 per cent.) placed upon water or various concentrations of alkali. "Spontaneous emulsification did not occur with nujol placed upon sodium palmitate solution. This shows that preformed soap is not an emulsifiant but is merely a stabilising or protective agent for droplets that have been formed by some other means. To be active it must be forming or diffusing."

W/O emulsions were also noted by McBain and Woo. One example may be quoted : "Nujol containing a slight amount of glycerine, placed upon water, spontaneously becomes turbid through formation of a water-in-oil emulsion which settles, without breaking, in 3 or 4 days. The water layer remains clear throughout. It is tempting to suggest that this is due to the diffusion of water being much faster than that of glycerine, resulting in a new type of osmosis and a suggested mechanism of myelin swelling."

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[1] *Trans. Faraday Soc.*, **36**, 651 (1940).
[2] *Proc. Roy. Soc.*, **A.**, **163**, 182 (1937).

Schulman and Cockbain's thesis adds to the necessity of a very low interfacial tension the factors of a stable interfacial molecular complex in the liquid condensed state, with the oil globule as a whole electrically charged (see p. 212).

REACTION VELOCITY AT A DINERIC INTERFACE

A very interesting investigation has been conducted by Bell[1] upon the velocity of reaction in a heterogeneous system consisting of two immiscible liquids. The reaction was between two substances *a* and *b* in two immiscible solvents A and B, *a* being insoluble in B and *b* being insoluble in A. Here the reaction must occur at the boundary of the two phases, thus depending on the formation of adsorbed interfacial films. For simplicity one reactant was an electrolyte in aqueous solution and the other was a non-electrolyte in a non-dissociating solvent ; the former gives a slight negative adsorption and the latter a positive adsorption. The reaction is thus only possible if the ions of the electrolyte strike the adsorbed film of the non-electrolyte.

Whilst such a reaction must be a true surface reaction, the influence of the rate of diffusion of the non-electrolyte to the interface cannot be ignored. Such an instance would result if the adjustment of adsorption were slow compared with the rate of removal of molecules from the boundary layer by reaction. Stirring would greatly affect this case, whereas it would be without influence if the reaction velocity is only a function of the equilibrium condition of the film. Solvents of widely different densities must be used in order to avoid disturbance of the dineric interface by stirring.

Bell chose as the reaction the oxidation of benzoyl-*o*-toluidine in benzene solution to benzoyl-anthranilic acid, by a neutral aqueous solution of $KMnO_4$, saturating each solvent with the other before use. He found that the reaction velocity was independent of the rate of stirring, *i.e.*, independent of the rate of diffusion of either reactant towards the interface. Further, he showed that the velocity is directly proportional to the concentration of $KMnO_4$, and, since he used dilute solutions, to the rate at which the ions strike the interface. Whereas ordinary diffusion reactions have a very small temperature coefficient, the present reaction velocity had a large temperature coefficient.

Measurements of the interfacial tension between water and benzene solutions of benzoyl-*o*-toluidine were made by the drop-weight method, and it was noted that it became constant for all concentrations exceeding about 5–6 grm. per litre. Since the reaction velocity was the same for all benzoyl-*o*-toluidine solutions having concentrations above this limit, it is concluded that the experiments provide an independent verification of the presence of a saturated monomolecular adsorbed layer at the surface of a concentrated solution of a non-electrolyte.

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[1] *J. Phys. Chem.*, **32**, 882 (1928). The reaction between benzyl chloride and water, two immiscible liquids, has been investigated by Titani and Kurano, *Bull. Chem. Soc. Japan*, **6**, 152 (1931).

SAPONIFICATION

The importance of the emulsion condition in technical practice is illustrated in the process of saponifying oils and fats. Treub [1] has pointed out that the chemical reaction occurring during saponification may theoretically take place : (*a*) in the fat phase, (*b*) in the aqueous phase, (*c*) in the interface : fat/aqueous phase. His experiments prove that saponification does occur in the dineric interface, the velocity of saponification increasing as the interface is extended, *i.e.*, as emulsification progresses. The value of emulsifying agents in this connection is discussed by Lewkowitsch,[2] Hoyer,[3] Walker,[4] Sandelin,[5] McKie and Lewis [6] and others.[7]

The rate of saponification of arachis oil has been observed [8] to increase with the degree of dispersion of the oil, with increase in volume of the oil phase and with increase in the quantity of emulsifying agent (arachis oil soap). An increase in the amount of alkali beyond that equivalent to the oil was without effect ; in fact, excess of alkali is harmful, as it causes de-emulsification. Dilution with water decreased the saponification, whereas alcohol was beneficial. According to Roshdestvenskii,[9] the speed of saponification of the various fats is inversely proportional to their content of unsaturated glycerides. He found that catalysts, such as certain aromatic hydrocarbons, greatly increased the speed. Lascaray,[10] too, found that the velocity was inversely proportional to the content of unsaturated glycerides. He states that the reaction occurs exclusively at the oil/water interface and he discusses his results in the light of the Harkins orientation ideas.

Weston [11] found that the presence of colloidal clay facilitated saponification owing to its emulsifying properties, and Fryer [12] patented its use. Tefs [13] investigated the problem, saponifying oils with 2N.NaOH, with and without the addition of 1 grm. of colloidal clay per 10 grm. of oil. Table 9 gives some of the results obtained.

Langton [14] investigated the saponification of tallow, palm oil, linseed oil, whale oil and palm kernel acid oil by steam autoclaving, CaO or

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[1] *Proc. Roy. Acad. Amsterdam*, **20**, 35 (1917) ; *Verslag. Akad. Wetenschappen Amsterdam*, **25**, 872 (1917) ; *J. chim. phys.*, **16**, 107 (1918) ; *Proc. Acad. Aci. Amsterdam*, **20**, 343 (1918).

[2] " Oils, Fats, and Waxes," 5th Edn., Vol. I., 83–86.

[3] *Z. deut. Öl-Fett-Ind.*, **41**, 113 (1931).

[4] *J. Chem. Soc.*, **119**, 1521 (1921).

[5] *Chem. Zentr.*, **93**, (iv), 508 (1922).

[6] *Chem. Met. Eng.*, **24**, 969 (1921).

[7] Lederer, *Z. deut. Öl-Fett-Ind.*, **45**, 749 (1925) ; *Allgem. Öl-Fettztg.*, **27**, 114 (1930).

[8] Speers *et al.*, *J. chim. phys.*, **30**, 414 (1933).

[9] *Seifensieder-Ztg.*, **55**, 127, 166 (1928).

[10] *Seifensieder-Ztg.*, **52**, 191 (1925); *Z. deut. Öl-Fett-Ind.*, **46**, 737, 753, 769 (1926); *Rev. gén. colloides*, **6**, 32 (1928).

[11] *Chem. Age (London)*, **4**, 604, 638 (1921).

[12] Brit. 166,971 (1920).

[13] *Z. deut. Öl-Fett-Ind.*, **46**, 801 (1926).

[14] *J. Oil Colour Chemists' Assoc.*, **5**, 41 (1922) ; *J. Soc. Chem. Ind.*, **42**, 51 T. (1923).

TABLE 9

INFLUENCE OF CLAY EMULSIFIER UPON SAPONIFICATION

Oil.	Degree of Saponification.	
	Without Clay.	With Clay.
	Per cent.	Per cent.
Cottonseed oil	59	100
Linseed oil	60·2	100
Soya bean oil	91	100
Palm oil	85·4	93·9
Using IN.NaOH, the results were :		
Whale oil	68·3	75·0
Tung oil	59·2	82·8
Japanese fish oil	59·2	82·8

MgO being present. Curves were plotted, ordinates being the percentage of free acid liberated, and abscissæ the time elapsing in hours. The curves are exponential in type, a slow initial stage being followed by a rapid second stage when about 90 per cent. of the fat is saponified in the first few hours ; subsequently, the rate of reaction slows down considerably. Langton finds herein strong support for Treub's views : " For, if the reaction be effected at the surface of contact of the two phases, then the increase of velocity of saponification at the beginning is easily explained. The emulsion of aqueous alkali and triglyceride is at first hardly dispersed, but in proportion as the saponification progresses, the concentration of the soap in the aqueous phase increases, thus diminishing the interfacial tension between the two phases and rendering the emulsion more and more dispersed. Thus the surface in which the reaction takes place becomes enlarged during the reaction itself, leading thereby to the acceleration which is indicated in some of the curves."

McBain [1] and co-workers have used the hydrogen electrode in their investigation of the rate of saponification of oils and fats by aqueous alkali. It was found that a given amount of soap possesses a limited emulsifying action, owing to the fact that the dineric interface is not proportionately increased when the volume of oil is doubled. Only a portion of the oil is emulsified, the remainder settling out immediately on standing. For a constant oil content, the rate of saponification increases with increasing soap content, since the amount of oil emulsified is increased.

The outstanding contribution in this field is due to McBain and Kawakami,[2] who emphasise that the chemical individuality of the liquid emulsified is important. Their paper is entitled : " The Influence of Physical State of a Soap Solution upon the Rate of Saponification of

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[1] *J. Chem. Soc.*, **121**, 1362 (1922) ; *J. Phys. Chem.*, **31**, 131 (1927).
[2] *J. Phys. Chem.*, **34**, 580 (1930).

Triglycerides and the Differing Degrees of Emulsification for Neighbouring Triglycerides."

A surprising and highly specific effect of the exact length of long hydrocarbon chains was revealed, neighbouring triglycerides in homologous series showing very different degrees of emulsification under identical conditions. The emulsifying capacity of ordinary aqueous soap solutions upon addition of NaCl exhibits the same striking maximum as does the viscosity.

"In a quantitative determination of the separate factors which govern the rate of saponification of oils and fats by aqueous alkali, it is found that no matter how complicated the system, the rate is almost exactly proportional to the concentration of hydroxyl ions. For the rest, it is almost entirely dependent upon the degree of emulsification of the oil. This depends upon the state of the aqueous alkaline soap solution, which in its turn is governed by the total amount of electrolyte. Neat soap is the best emulsifying agent, especially in the presence of the maximum amount of salt which can be added without graining out the soap, but insoluble, fully grained out curd fibres are also good."

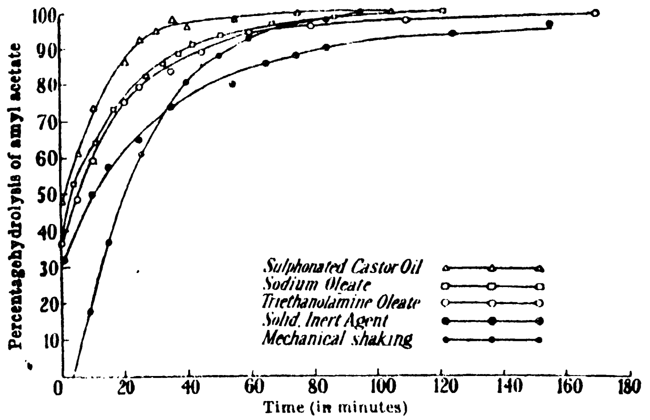

FIG. 12.

King and Mukerjee[1] have pointed out that in reactions where one of the products is itself an emulsifying agent, the original stabilising agent may be reinforced or opposed to the new product. To avoid such complication these workers studied the hydrolysis of amyl acetate by alkali. Here neither reactants nor products are surface-active and they permit an investigation of the influence of different emulsifying agents.

Since the adsorbed film at the liquid/liquid interface in an emulsion often possesses considerable mechanical strength, one cannot infer that the interface in an emulsion is a free boundary across which the two immiscible components can interact. "It must be expected that the chemical nature of the emulsifying agent will be of great importance, as this will control the diffusion of the reactants across the interface even if the adsorbed film is chemically inert. Normally, reaction will be much slower than at the equivalent area of free interface, but it is conceivable that in some cases it might be accelerated by a catalytic effect occasioned by interfacial adsorption."

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[1] *J. Soc. Chem. Ind.*, 57, 431 (1938)

For the hydrolysis of amyl acetate 25 c.c. of the ester were added to 200 c.c. of 0·25N NaOH and 25 c.c. of water, stored at 20° C. and the reduction of alkali determined by titration. When emulsifying agents were employed 1 per cent. was used, added in aqueous solution or suspension.

Fig. 12 reproduces typical results. For each example a size frequency analysis was made of the emulsion and the area of interface per unit weight of ester calculated. These areas, together with the time of three-quarter change to demonstrate the specific effects of the emulsifying agents are collected in Table 10.

TABLE 10

No.	Agents	Time of 3/4 change, min.	Area of interface per g. of ester, sq. cm.	Time of 3/4 change per unit area, min.
1	None	2220	3·7	8,214
2	None (mechanically shaken) . . .	29·5	—	—
3	Triethanolamine oleate	17	7,185	122,145
4	Sulphonated castor oil	9	7,389	66,501
3	Sodium oleate	15	9,712	145,680
6	Solid, inert agent	30	1,912	57,360

"It is immediately obvious that emulsification has enormously increased the rate of hydrolysis from 37 hours to a few minutes. On the other hand, vigorous mechanical shaking produces a result of the same order, although not quite so satisfactory as that from efficient emulsification. Visual examination shows that mechanical agitation does not break up the ester nearly as much as does true emulsification, but the extended interface is free, in contrast to the emulsions where the relatively much larger interface is blocked by the presence of the emulsifying agent. Thus in experiment 6 the interfacial area was probably many times greater than in mere mechanical shaking, but the inert solid adsorbed at the interface prevented free access of the reacting liquids so that the actual area of interface, and hence rate of reaction, was smaller.

As already indicated, previous authors have clearly demonstrated that with a given emulsifying agent the rate of reaction is proportional to the area of interface ; the present results indicate that when different agents are employed this is no longer strictly the case. Thus an emulsion of amyl acetate in alkali, stabilised by sulphonated castor oil, was hydrolysed much more rapidly than the corresponding emulsion with sodium oleate, which was considerably finer. This is probably due to the acid nature of the sulphonated castor oil which would tend to attract alkali to the interface, where it would react to hydrolyse the ester.

In the last column of Table 10, the time of three-quarter change is multiplied by the area of interface per unit weight of ester to give a value which represents the time of reaction per unit area of interface. It is thus possible to compare the specific influences of the different agents on the rate of reaction, assuming uniformity of emulsification. It is clearly evident that reaction takes place much more quickly at the free, unemulsified interface. Of the emulsions, the coarse solid-stabilised example allows quickest reaction. This is probably because of the incomplete nature of the interfacial film formed by small solid particles. Next in efficiency amongst the emulsions is that stabilised by sulphonated castor oil, followed by triethanolamine oleate and finally by the more alkaline sodium oleate."

CHEMICAL REACTIONS WITH EMULSIONS

Chemical reactions may be greatly accelerated by the creation of an extensive oil/water boundary, and the patent literature reflects this fact with several good examples.

Von der Heide [1] hydrogenates oils and fats by adding them in emulsion form to cultures of hydrogen-producing bacteria, adding also nitrogenous substances such as urea. The vulcanisation of oils such as linseed oil containing a considerable proportion of unsaturated groupings is carried out [2] at 160°–170° C. by the action of sulphur on the oil emulsion, using casein, NH_3 and NH_4 oleate as emulsifying agent. The polymerisation of unsaturated oils [3] is carried out in emulsions or they may be polymerised with unsaturated hydrocarbons in the presence of oxygen or oxygen-splitting compounds, if desired with heating. Thus, linseed oil, butadiene and oleic acid, emulsified in water by the aid of Turkey-red oil, is polymerised in the presence of Bz peroxide at 60° C. in a closed vessel. The products are employed directly or after coagulation for rubber latex mixtures.[4] Again, water-insoluble derivatives of acrylic and a-methylacrylic acid, or their mixtures, are emulsified and subjected to known polymerisation methods to yield an artificial latex-like product.[5]

Many patents relate to the preparation of synthetic rubber by the polymerisation of emulsified dienes.[6] These have been enumerated by Whitby and Katz,[7] who mention the advantages gained by this technique. Important Russian work has been summarised in 1936.[8] Polymerisation of butadiene to synthetic latex takes place when technical butadiene (65–85·7 per cent. butadiene and 14–24 per cent. β-butylene) in aqueous emulsion, ammonia and oleic acid are heated in the presence of a polymerisation catalyst (peroxides, diazoaminobenzene, etc.) in a rotating sealed glass tube at 40°–70° C. for several days. The course of the polymerisation was followed by noting the decrease in the total volume of the system and the increase in viscosity both phenomena being directly related to the degree of polymerisation. The synthetic butadiene latex was characterised by great stability due to the minute size of the dispersed particles.

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[1] Ger. 482,919 (1926).

[2] I.C.I. Ltd., and Naunton, Brit. 413,252 (1928).

[3] I.G. Farbenind. A.-G., Ger. 563,202 (1929).

[4] I.G. Farbenind. A.-G., Brit. 362,845 (1930).

[5] I.G. Farbenind. A.-G., Brit. 358,834 (1930).

[6] Thus: I.G. Farbenind. A.-G., Ger. 526,304; 526,305; 526,498 (1928); Luther and Heuck, U.S. 1,896,491 (1933); McAllister, Brit. 514,043; 514,081 (1939).

[7] *Ind. Eng. Chem.*, **25**, 1338 (1933).

[8] Dogadkin *et al.*, Russ. 46,354 (1936); *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. chim.*, **1936**, 397–435; *Colloid J.* (*U.S.S.R.*) **3**, 129 (1937).

Peculiar effects were observed for the influence of different emulsifying agents on the course of the polymerisation. Proteins, such as casein and albumin, retarded the polymerisation process, but the action of other emulsifying agents which did not exert a specific influence on the mechanism of the polymerisation was determined primarily by their surface activity. Both the yield of polymer and the rate of polymerisation were markedly increased by raising the *p*H of the medium.

Considerable attention has been given to the polymerisation of aqueous emulsions of 2-halo-1, 3-butadiene.[1] One process employs as emulsifying agent an inorganic salt of an organic base of high molecular weight such as stearylpyridinium bromide.[2] Dispersion may also be effected in glycerol, ethylene glycol or formamide.[3] Mixed polymerisation of the halo-butadiene is claimed [4] with an ester, halide or ether of vinyl alcohol or a vinyl ketone or acrylic, methacrylic or itaconic acid or an ester of one of these acids. For example, 2-chloro-1, 3-butadiene is polymerised with vinyl butyrate in aqueous emulsion in the presence of Bz peroxide with the use of partially saponified polyvinyl acetate as emulsifying agent.

Interpolymerisation products are prepared by polymerising in aqueous emulsion any desired pair of vinyl or acrylic compounds having different speeds of polymerisation, in any desired ratios, by adding during the polymerisation the compound having the higher speed in small fractions or continuously, at about the rate at which it is used up by the interpolymerisation, to the compound having the lower speed. Thus, vinyl chloride is emulsified in an aqueous solution of HCOOH, H_2O_2, and Na α-hydroxyoctodecanesulphonate, and methyl acrylate is added in portions during the polymerisation, the polymer being coagulated by aluminium sulphate, heated with aqueous NaOH, washed and dried.[5]

The formation of stable, highly disperse aqueous systems of vinyl resins is claimed by polymerising acrylic ester aqueous emulsions in the presence of Na acrylate to form a polyacrylic ester with a COONa group.[6] 2-vinylfuran may be polymerised in emulsion state.[7] As suitable emulsifying agents are claimed [8] methylcellulose, partial esters, ethers or acetates of polyvinyl alcohols, such as partially saponified polyvinyl acetate.

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[1] Brit. 387,340 (1933); Calcott and Youker, U.S. 2,161,949 (1939).

[2] E. I. du Pont de Nemours and Co., Brit. 461,279 (1937), U.S. 2,088, 407 (1937).

[3] Carothers, U.S. 2,080,588 (1937); Dales and Downing, U.S. 2,080,561 (1937).

[4] Chemische Forschungsgesellschaft m.b.H., Brit. 469,976 (1937).

[5] I.G. Farbenind. A.-G., Brit. 466,898 (1937).

[6] Röhm and Haas A.-G., Brit. 437,446 (1935); Fr. 789,166 (1935); I.C.I. Ltd., Fr. 844,091 (1939); 842,930 (1939); I.G. Farbenind. A.-G., Fr. 798,036 (1936); 798,056 (1936); 797,686 (1936); 814,093 (1937); E. I. du Pont de Nemours and Co., Brit. 437,284 (1935); Fr. 842,829 (1939); Pavlovich, *J. Applied Chem.* (*U.S.S.R.*), **10**, 1071 (1937).

[7] I.G. Farbenind. A.-G., Fr. 830,122 (1938).

[8] Chemische Forschungsgesellschaft m.b.H., Fr. 801,034 (1936). Cf. Starck and Freudenberger, U.S. 2,227,163 (1940).

AQUOLYSIS

Another instance of the application of the extended oil/water interface is found in aquolysis, or the conversion of petroleum oil by water to lighter products such as gas. White [1] emulsifies a heavy oil such as gas oil with several volumes of water and subjects the emulsion to temperatures and pressures above the critical point. Ellis [2] specifies the temperature as about 540° C. and the pressure as about 3,000–3,500 lb. Now follows cooling to a temperature slightly below the critical for water while maintaining pressure by which separation of oil from liquid water is effected. It is advantageous to include gas [3] in the emulsion as by aeration [4] or charging with CO_2, each globule of gas being coated with a film of water within a film of oil.[5]

The Hoffmann fat splitting may be cited here. It is a continuous process which combines fat splitting and distillation of fat acids. The fat emulsion is passed through a splitting zone at 220°–260° C. under 20–60 atm. pressure.[6]

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[1] U.S. 1,956,603 (1934). See also Haslam. U.S. 1,956,573 (1934); McKee, U.S. 2,028,795 (1936); Wade, Can. 355,867 (1936); Russell, U.S. 2,059,535/6 (1936).

[2] U.S. 1,956,567 (1934). Cf. Dubbs and Morrell, U.S. 1,744,109 (1930).

[3] Gas Fuel Corp., Fr. 744,602 (1933); Brit. 410,773 (1934).

[4] Gas Fuel Corp., U.S. 1,970,996 (1934).

[5] Russell, U.S. 1,970,771 (1934).

[6] Hoffmann, *Ole, Fette, Wachse, Seife, Kosmetik* **1936**, (xiii), 4–16.

CHAPTER III

DILUTE EMULSIONS AS OIL HYDROSOLS

Two pure immiscible liquids, *e.g.*, an oil and water, when shaken together or otherwise agitated, will temporarily produce an emulsion, but as soon as agitation ceases, the drops of the respective liquids (both liquids become subdivided) coalesce, and separation into layers occurs. By suitable treatment fairly stable emulsions of a pure oil in water may be obtained, but the concentration of the oil is very low indeed. Thus, engine condenser water frequently contains very fine oil globules, forming a stable emulsion in which the concentration of oil is about 1 in 10,000. Refluxing oil with water will yield a similar emulsion. More concentrated emulsions are possible when the powerful dispersion effect of ultrasonic waves is employed (see p. 362). Thus, Bondy and Söllner[1] obtained temporary emulsions in which toluene was dispersed in distilled water to a phase volume of 4·5 per cent. The diameters of the globules ranged from 2μ to 10μ, the highly dispersed emulsions forming when the time of radiation was short and the energy small, factors tending to limit the coagulation influence of the irradiation.

Until recently, following Groschuff[2] and Heymann,[3] it was accepted that with only water and oil, both pure, the dilute emulsion would always be of the O/W type. However, Cheesman and King[4] have reported that cyclic ketones, such as cyclohexanone and acetophenone, form W/O emulsions with water. "The composition of cyclohexanone and acetophenone, the only substances which have so far been observed to possess these remarkable properties, would suggest that the ketone group itself provided a hydrogen ion after undergoing keto-enol transformation." Whilst this tentative explanation may hold for the special systems investgated, other explanations may have to be sought for any further examples found of water oleosols. With the data of Seifriz in mind (see p. 244) one would anticipate W/O emulsions possible with water and certain higher fractions of hydrocarbons.

It is pertinent here to refer to the work of Carruthers[5] on the stability of dispersions. By mechanical homogenisation in the cold he found that such compounds as octadecane, octadecanol, and octyl bromide were dispersed in water with a life of at least 24 hours, whilst hexane, chloroform, carbon tetrachloride, bromoform, benzene, and amyl alcohol gave only transient dispersions. The two groups differ chiefly in that the non-emulsifiable compounds have low boiling-points and small molecules, whilst the emulsifiable compounds have high boiling-points and large molecules.

It is suggested by Carruthers that the instability of the dispersions of the non-emulsifiable compounds is due to a surface liability which in the limit governs the volatility of the dispersed phase. Although there is a charge on the particles, the surface molecules of the droplets which carry the charge are rapidly removed by evaporation and the system is unstable. Again, ions, although capable of being adsorbed by a stable surface such as is presented by the long chain molecules, cannot be adsorbed by the surface made up of labile molecules in constant agitation.

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[1] *Trans. Faraday Soc.*, **32**, 556 (1936).

[2] *Kolloid-Z.*, **9**, 257 (1911). See also Hall, *J. Phys. Chem.*, **21**, 609 (1917).

[3] *Ibid.*, **52**, 279 (1930). See Harkins and Beeman, *J. Am. Chem. Soc.*, **51**, 1691 (1929).

[4] *Trans. Faraday Soc.*, **36**, 246 (1940).

[5] *Ibid.*, **34**, 646 (1938).

THE SIZE OF PARTICLES

The oil globules in pure oil-in-water emulsions have diameters of the order of 10^{-5} cm., as for colloidal suspension. Donnan,[1] investigating the stability of colloidal solutions and emulsions in relation to surface tension, on thermo-dynamical considerations, predicted a critical diameter of particle when one phase is very finely divided in the other. The order of magnitude expected is 10^{-5} cm.

Lewis [2] demonstrated in approximate manner the existence of this critical or equilibrium size of globule in the case of several emulsions of oil in water. By shaking a purified mineral oil in water for forty-eight hours he obtained an emulsion (whose maximum oil content was 2 per cent.) in which the oil globules had a diameter of 4×10^{-5} cm., a value of the same order as found by Burton [3] for colloidal metals. Lewis now prepared emulsions by (*a*) boiling oil and water together under a reflux condenser for 30 hours, producing partial emulsification ; (*b*) pouring an alcoholic solution of oil into water, producing a milky emulsion [4] ; and (*c*) steam-distilling aniline, forming an unstable emulsion of aniline in water. In all cases the drops possessed diameters of the order of 10^{-5} cm. Similarly, Tuorila [5] prepared a hydrosol of paraffin (M.P. 68°–70° C.). He saturated 100 c.c. of 96 per cent. alcohol at 60° C. with the paraffin and added this solution by drops to very pure water ; boiling removed the alcohol. The cooled emulsion was filtered through a coarse filter and made up to 1 litre with water. The hydrosol contained 1·66 per cent. of paraffin and 1 c.c. contained $104 \cdot 7 \times 10^8 \pm 3 \cdot 56 \times 10^8$ globules, the average radius being 0·724 μ. Some of the globules were about 10 μ and others were as fine as 0·1 μ.

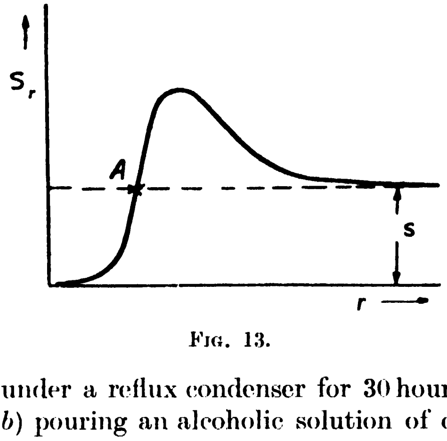

FIG. 13.

Lewis [6] has discussed the limiting size of emulsion globules in relation to interfacial tension, and electric charge. Assuming the globules are isolated charged spheres, the charge being independent of the size, the opposing effects of interfacial tension and electric charge can be equated and the relation holds :

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[1] *Z. physik. Chem.*, **46**, 197 (1903) ; cf. *ibid.*, **37**, 735 (1901).

[2] *Kolloid-Z.*, **4**, 211 (1909).

[3] *Phil. Mag.*, **11**, 425 ; **12**, 472 (1906).

[4] Cf. Palmitic acid hydrosols prepared by Mukherjee, *J. Indian Chem. Soc.*, **14**, 129 (1935).

[5] *Kolloidchem. Beihefte*, **27**, 55 (1928).

[6] *Kolloid-Z.*, **5**, 91 (1909).

$$r = \sqrt[3]{\frac{e^2}{16\pi\sigma K}},$$

where r is the radius of a globule, e the electric charge, K the dielectric constant, and σ the interfacial tension between the oil and water. When this equilibrium is realised, the effect of curvature on solubility ceases, and the globules can remain in equilibrium with a plane surface. Knapp[1] has extended these considerations and shown that, if S_r be the solubility of a colloid particle of radius r, and S the usual or normal solubility, then

$$S_r = S\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}} \quad . \quad . \quad . \quad . \quad \text{(I.)}$$

when α and β are constants and equal to $\frac{2\sigma M}{RTd}$ and $\frac{e^2 M}{8\pi KRTd}$ respectively, where M = the molecular weight of the dispersed phase, R the gas constant, T the absolute temperature, d the density of the dispersed phase, and e the electric charge.

By differentiation,

$$\frac{dS_r}{dr} = S\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}}\left(\frac{4\beta}{r^5} - \frac{\alpha}{r^2}\right) \quad . \quad . \quad . \quad \text{(II.)}$$

which is equal to zero when

$$r = \sqrt[3]{\frac{4\beta}{\alpha}} = \sqrt[3]{\frac{e^2}{4\pi K\sigma}} \quad . \quad . \quad . \quad \text{(III.)}$$

When r has this value, the second differential of (II.) becomes negative, so that there is a maximum solubility at this point. When r approaches zero, S_r approaches zero ; when r is infinite, S_r is equal to S. These results are expressed by Knapp as a graph in Fig. 13.

In making emulsions the dispersed phase is present, both as large masses and small globules. The drops increase or decrease in size until their solubility becomes the same as that of the mass in bulk, which possesses an approximately plane surface.

For a particle with a finite radius to be in equilibrium with a flat surface the solubility must be equal to S. From equation (I.) this value for S_r is given when

$$\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}} = 1,$$

that is, when

$$\frac{\alpha}{r} - \frac{\beta}{r^4} = 0,$$

or

$$r = \sqrt[3]{\frac{\beta}{\alpha}} = \sqrt[3]{\frac{e^2}{16\pi K\sigma}}.$$

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[1] *Trans. Faraday Soc.*, **17**, 457 (1922). Similar considerations are advanced by Defay *Bull. sci. acad. roy. Belg.*, **20**, 559 (1934). See also Bradley, *Trans. Faraday Soc.*, **36**, 392 (1940) on : "The Influence of Interfacial Curvature on Solubility."

This equilibrium value of the radius is shown in the graph as the ordinate of the point A.

For the further mathematical treatment of the subject, especially in relation to the question of electrical double-layer effects, Knapp's paper should be consulted.

THE CONCENTRATION OF EMULSIONS

It has already been remarked that, for pure oil and water, 2 per cent of oil is the maximum amount that can ordinarily be emulsified in water.[1] Theoretically, if the oil globules be considered as rigid spheres of equal diameter, it should be possible to pack them together in such a way that each sphere will touch twelve others. This maximum packing—*i.e.*, concentration—occurs when about 74 per cent. of the total available space is occupied by the spheres. Hence approximately 74 per cent. of oil can theoretically be dispersed in about 26 per cent. of water.[2] For deformable spheres, such as the oil globules really are,[3] flattening of the spheres can occur at the points of contact, and polyhedral forms ensue. In fact, experiments have shown that stable emulsions containing even 99 per cent. of the disperse phase may be obtained.[4]

Such concentrated emulsions, however, demand the presence of a third substance, capable of forming an adsorbed film at the oil/water boundary. The theoretical case of 74 per cent. pure oil being dispersed in 26 per cent. pure water has never been realised, and neither has the reverse case. The 2 per cent. limit obtained by Lewis is bound up with the whole vexed question of saturation-concentration in colloidal systems generally. At the present time our knowledge of the actual mechanism of colloidal solubility, whether for emulsions, suspensions, or so-called colloidal solutions, is insufficient to account for the fact that, in general, pure two-phase systems only seem to be stable over low concentration ranges.[5]

BROWNIAN MOVEMENT IN EMULSIONS

Suspensions of fine particles, fine-grained emulsions, and colloidal solutions of metals, hydroxides and sulphides all show, when examined under the ultramicroscope, that the particles of the dispersed phase are in continuous zigzag motion. The phenomenon is termed the Brownian motion, after Brown,[6] who studied the movements of pollen grains in water. It is now agreed that the movements of finely-divided particles suspended in liquids is due to the bombardment of the particles by the molecules of the surrounding liquid.[7]

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[1] Wiegner was only able to disperse a maximum of 0·02 per cent. of olive oil in distilled water; *Kolloidchem. Beihefte*, **2**, 213 (1910).

[2] See p. 143.

[3] Cf. Hatschek, *Kolloid-Z.*, **7**, 81 (1190).

[4] Pickering, *ibid.*, **7**, 11 (1910).

[5] For a fuller discussion on saturation in colloid solutions, see Ostwald, "Handbook of Colloid Chemistry" (London, 1919), pp. 132 145.

[6] *Phil. Mag.* **4**, 161 (1828); **6**, 161 (1829).

[7] For most recent work see Fürth, *Kolloid Z.*, **42**, 197 (1927); Hire, *Phys. Rev.*, **52**, 325 (1937); Kappler, *Naturwissenschaften* **27**, 649; 666 (1939): Simha, *J. Phys. Chem.*, **44**, 25 (1940); Ehrenhaft, *Phys. Rev.*, **57**, 1050 (1940); Duclaux, *J. phys. radium* (8), **1**, 81 (1940); and especially Cox, *Reports on Progress of Physics*, **5**, 9 (1939). A mathematical account is given by Niessen and Bakker, *Physica*, **5**, 977 (1938).

The Brownian motion does not begin in suspensions until the diameters of the particles are reduced to below 3 to 5 μ.[1] As the particles decrease in size under constant conditions the Brownian movements become more rapid, and translatory or progressive motion is apparent. Exner[2] examined guttapercha dispersions at 23° C., and obtained the following figures for the dependence of the Brownian motion on the size of particles :—

Diameter of Particles.		Velocity of Particles.
1·3 μ	.. ..	2·7 μ per second.
0·9 μ	.. ..	3·3 μ ,,
0·4 μ	.. ..	3·8 μ ,,

For a gamboge suspension he found that a variation in the diameter from 0·4 μ to 1·3 μ altered the velocity from 3·8 μ to 2·7 μ per second. At 3 μ the motion was hardly perceptible, whilst at 4 μ it was *nil*.

Working with an emulsion of olive oil in water, with gelatose as emulsifying agent, Seifriz[3] observed that the oil globules of 1 μ to 2 μ diameter were in active Brownian motion, but this was very sluggish for globules of 3 μ diameter.

The Brownian movement has been the subject of numerous investigations[4] and has played a most important part in proving the real existence of molecules.[5] In the present volume, however, it is only mentioned as a property of emulsions. Whenever emulsions are treated so that the globules coalesce to particles whose diameters exceed 4 μ, the Brownian motion ceases. Thus Henri[6] found (using the cinematograph) that, when a rubber emulsion is treated with acetic acid, the motion slows down before coagulation actually occurs, whereupon it ceases altogether. In general, Brownian motion is believed to cease when the iso-electric (electrically neutral) point is reached.

The slowing down of Brownian motion presupposes an increase in the size of the globules, probably due to adsorption. Svedberg[7] found that with sufficiently dilute suspensions, the presence of electrolytes did not interfere with Brownian motion. In more concentrated suspensions (or emulsions) the electrolyte enables coalescence of particles to occur and the increased size of the resulting unions slows down the Brownian motion. (Coagulation[8] of colloid suspensions in general depends on the probability of collisions, *e.g.*, due to Brownian motion, and the probability of adhesions, influenced, *e.g.*, by electric charge.)

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[1] Wiener, *Pogg. Ann.*, **118**, 79 (1863).

[2] *Ann. Physik.*, **2**, 843 (1900).

[3] *J. Phys. Chem.*, **29**, 746 (1925).

[4] See the excellent account in Burton's "Physical Properties of Colloidal Solutions" (London, 1921), Chapter IV. The theory of Brownian Motion is treated by : Uhlenbeck and Ornstein, *Phys. Rev.*, **36**, 823 (1930) ; Ornstein and van Wijk, *Physica*, **1**, 235 (1934) ; Satô, *Z. Physik.*, **86**, 667 (1933) ; Barnes and Silverman, *Rev. Modern Physics*, **6**, 162 (1934) ; Brumberg and Vavilov, *Z. Physik.*, **73**, 833 (1932) ; Métadier, *Compt. rend.*, **197**, 29 (1933). Satô deals with "The Representation of Brownian Motion" in *Science Repts. Tohoku Imp. Univ.*, 1st Ser., **22**, 599 (1933).

[5] Perrin, *Kolloidchem. Beihefte*, I. (1906).

[6] *Bull. Soc. Fr. Phys.*, **4**, 45, 61 (1908) ; cf. Hauser, *Ind. Eng. Chem.*, **18**, 1146 (1926).

[7] *Nov. act. reg. Soc. Scient. Upsal.* (4), **2**, No. I., pp. 146–55.

[8] *Vide* Kruyt, "The Mechanism of Coagulation," in Alexander's "Colloid Chemistry" (New York, 1926), Vol. I., 306–22.

ELECTRICAL BEHAVIOUR OF EMULSIONS

Fundamental in the physical chemistry of emulsions, particularly the oil hydrosols, are the considerations of the electric charge on the globules, the cataphoresis of the globules, the electrical conductivity of emulsions and the dielectric constants of emulsions. (On the technical side the importance lies in the effect of high potential current on crude petroleum (W/O) emulsions, whilst electrical methods are commonly employed to remove oil from industrial effluents and from boiler-feed water. Much attention, too, is being paid to the electric deposition of rubber from latex.)

To a large extent the discussion relates to hydrosols in general, the oil hydrosols merely representing special cases. Thus, the so-called electrokinetic potential and the phenomenon of a critical potential in the coagulation of a colloid system concern general colloid chemistry. Oil hydrosols, however, offer peculiar advantages for investigation, being easily reproducible, as well as possessing the dispersed phase in spherical form.

THE ELECTRICAL DOUBLE LAYER

The oil globules in two-phase emulsions of oil in water carry a negative charge, as proved by cataphoresis tests. The origin of this charge is still under discussion, as is, indeed, the more general case of the electric charge of all colloid particles. For a time an empirical rule due to Coehn [1] was accepted, viz., that for two phases in contact, the phase with the higher dielectic constant assumes the positive charge. Apart from the fact that no clue is thereby given as to the origin of this charge, many exceptions to the rule are now established.

The electric charge has usually been simply ascribed to the adsorption of ions. In the case of emulsions carrying a negative charge, adsorption of OH' ions at the surface of the oil globules was postulated. Even when emulsions are made with absolutely pure oil and pure water there must be present $H^{\cdot}$ and OH' ions due to the ionisation of the water, and consequently adsorption of OH' ions can take place. The nature of the chemical forces to which such adsorption may be due has been treated in an important paper by Mukherjee.[2]

The adsorbed ions are considered to be concentrated near the surface of the globules in the layer of the liquid immediately bathing the globules. An equivalent amount of ions of opposite sign is necessarily postulated as being present in the liquid. The ions imparting the charge to the surface are situated wide apart from each other compared to molecular dimensions. The thickness of the double layer is much disputed.[3] The original value given by Helmholtz (IÅ) did not take into account the dielectric constant. Moreover, his experimental findings are open to criticism, and current opinion inclines to the view that the thickness of the double layer within the liquid medium is about 100 Å or 10 mμ.[1]

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[1] *Wied. Ann.*, **64**, 227 (1898); *Z. Elektrochem.*, **16**, 586 (1910). The modern interpretation is presented by Kanamaru and Takada, *Kolloid-Z.*, **86**, 77 (1939).

[2] *Trans. Faraday Soc.*, **16**, Appendix, 103 (1922); cf. Oakley, *J. Phys. Chem.*, **30**, 902 (1926); Chakravarti *et al.*, *J. Phys. Chem.*, **34**, 326 (1930).

[3] von Hevesy, *Kolloid-Z.*, **21**, 129 (1917); Bikerman, *Z. Elektrochem.*, **38**, 763 (1932); McClendon, *Science*, **66**, 200 (1927); Gouy, *J. de Phys.*, (iv.), **9**, 457 (1910); Abramson, *Colloid Symposium Monog.*, **11**, 287 (1935).

The two layers of oppositely-charged ions are commonly referred to as the *Helmholtz double layer.*[2] The oil globule and its double layer may be considered as a small condenser, a definite potential difference existing between the oil and the nearer ionic layer. Such a system should be self-contained and electrically neutral to an external electric field, and for this reason a certain "give" or "facility of slip" has been postulated between the nucleus and the outer ionic layer,[3] since the oil globules in emulsions wander to the anode in an electric field. Modern work, however, is against the idea of hydrodynamic slip, *e.g.*, it is contrary to the notion of orientation of surface molecules.

The Helmholtz double layer is, of course, not confined to emulsions. Indeed it is a universal accompaniment to the boundary or interface between two phases, no matter what their electrical or chemical natures, although the relative motion of the phases usually introduces the subject.[4]

ELECTRICAL MOVEMENTS IN COLLOID SYSTEMS

An extended discussion of electrical movements in colloid systems is beyond the scope of the present volume,[5] but because of certain newer views concerning the electrical double layer, attention must be directed to four common phenomena in two-phase, solid/liquid systems. (A) When a difference of potential leads to the passage of an electric current through the system, relative displacement of the phases may occur: (1) given the solid as a porous diaphragm, the liquid is forced through this (*electrical endosmose*); (2) given the solid as a suspension in the liquid medium, the solid particles migrate towards one of the electrodes (*cataphoresis*). (B) Relative displacement of the phases may produce a difference of potential so that an electrical current flows through the system: (3) forcing the liquid through the solid—porous diaphragm—leads to a potential difference, a current being set up between the extremes of the diaphragm (*streaming potential*); (4) the solid powder is dropped through the liquid medium, a potential difference being set up between the upper and lower liquid levels (*sedimentation potential*). All the above phenomena are grouped under the term electrokinetic phenomena and they are obviously very intimately related.[6] The common basis is the notion of an electrical double layer.[7]

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[1] McBain, *J. Phys. Chem.*, **28**, 706 (1924).

[2] *Wied. Ann.*, **7**, 337 (1879) and *Wissenschaftliche Abhandlungen*, **1**, 855 (1882). *Vide* Michaelis, "The Origin of the Electric Double Layer" in "The Effects of Ions in Colloidal Systems" (Baltimore, 1925), 28–50; Alexander's "Colloid Chemistry" (New York, 1926), Vol. I., 457; Kruyt, *Chem. Weekblad.*, **27**, 101 (1930), and "Colloids" (London, 1930), 96–115; von Smoluchowski, *vide* Graetz, "Handbuch der Elektrizität und der Magnetismus," Vol. II. (1914), 366.

[3] Lamb, *Phil. Mag.* (3rd series), **25**, 52 (1888).

[4] Cf. McBain and Foster, *J. Phys. Chem.*, **39**, 341 (1935). Cf. Verwey, *Rec. trav. chim.*, **53**, 933 (1934).

[5] *Vide* Freundlich, "Kapillarchemie" (Leipzig, 1930), Vol. I., 335–432; Briggs, *Brit. Assoc. Colloid Repts.*, **2**, 26–52 (1921). A full theoretical treatment is given by Abramson, "Electrokinetic Phenomena and Their Application to Biology and Medicine" (New York, 1934).

[6] Cf. Moyer, *J. Phys. Chem.*, **42**, 391 (1938).

[7] Urban, White and Strassner, *J. Phys. Chem.*, **39**, 311 (1935) and Monaghan, White and

ORIGIN OF THE DOUBLE LAYER

It is now agreed [1] that the origin of the electric double layer is to be sought in an unequal distribution of potential-determining ions. Such ions alone contribute to the building up of the inner sheath of the double layer and so function as peptising ions (giving a primary stability to dispersed hydrophobic particles). Hamaker [2] points out that such ions are strongly adsorbed at low concentrations ; pronounced adsorption at higher concentrations is ineffective.

Rideal [3] in his introduction to the recent general discussion on this subject outlined three methods which create the system of ion pairs according to the nature of the homogeneous phases in contact with the interphase : (1) when one phase is impermeable to ions, adsorption is responsible for the double layer (termed Gouy or specific adsorption) ; (2) one phase may be a conductor, permeable to electrons, and the ion pair system will originate by passage of a current across the interphase ; (3) one phase may be ionogenic and form ions soluble in the other phase, *i.e.*, the boundary is selectively permeable to an ion.[4]

DOUBLE LAYER ACCORDING TO HELMHOLTZ

The early work of Wiedemann [5] on electrical endosmose and cataphoresis was followed by Quincke's [6] suggestion that the contact of solid with liquid caused the electrical charge on the solid with an accompanying equal-magnitude charge of opposite sign in the liquid in the immediate vicinity of the solid. Helmholtz [7] mathematically developed this idea and was followed by Perrin,[8] Lamb [9] and von Smoluchowski.[10] The formulæ developed for the phenomena of electrical endosmose and cataphoresis respectively are :

$$V = \frac{r^2 \zeta E D}{4 \eta l}$$

and

$$v = \frac{\zeta E D}{4 \pi \eta l}.$$

Urban, *Colloid Symposium Monog.*, **11**, 263 (1935) point out that although the outer Helmholtz layer is not displaced by hydrostatic forces, it may nevertheless move in an electric field. Accordingly, only the outermost or diffuse component contributes to the stream potential, whereas both the diffuse and outer layers contribute to electrosmotic velocity.

[1] *Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions*, Utrecht, 1937, p. 11.

[2] *Ibid.*, p. 30.

[3] *Trans. Faraday Soc.*, **36**, 1 (1940). See also Gemant, *J. Phys. Chem.*, **43**, 748 (1939).

[4] Important summaries dealing with many aspects of the electric double layer are contained in *Cold Spring Harbor Symphosia on Quantitative Biology*, **1**, 1–38 (1933) ; Verwey, *Chem. Reviews*, **16**, 363–415 (1935) with 142 refs. ; *Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions*, Utrecht, (1937), p. 180 ; *Trans. Faraday Soc.*, **36**, p. 322 (1940) ; Butler : "Electrocapillarity" (London, 1940), Chaps. IV. and V.

[5] *Pogg. Ann.*, **87**, 321 (1852).

[6] *Ibid.*, **113**, 513 (1861).

[7] *Wied. Ann.*, **7**, 337 (1879).

[8] *J. chim. phys.*, **2**, 601 (1904) ; **3**, 50 (1905).

[9] *Brit. Assoc. Report* (1887), 495–510.

[10] *Bull. Acad. Sci. Cracovie* (1903), 182.

where v = volume of liquid carried per second through a capillary tube whose radius is r and length is l.
ζ = potential difference between the two layers of the Helmholtz double layer considered as a condenser.
E = the applied E.M.F.
D = the dielectric constant of the liquid.
η = coefficient of viscosity of the liquid.
v = cataphoretic velocity of solid moving through the stationary liquid.

It should be noted that in these equations no account is taken of the thickness of the double layer.[1]

The original idea of Helmholtz has been considerably modified in recent years. Helmholtz and Lamb assumed a double layer of fixed (molecular) dimensions, a condition which could arise if two ions of an electrolyte are adsorbed to different extents. The charged particle plus the double layer is thus an electrically-neutral entity, and under the influence of an applied E.M.F. *all* the ions in the outer layer participate in the movement. *There would be no mutual action between two such particles.* Again, as noted by Freundlich, a Helmholtz layer consisting of two parallel surfaces carrying ions of opposite sign would give rise to a potential difference defined solely by the magnitude of the charge and the geometric conditions. Having postulated the double layer Helmholtz referred to cataphoresis thus : " On the whole the algebraic sum of the two equals zero, and the centre of gravity of the complete system, solid particle and surrounding positively charged fluid layer taken together, cannot be moved by the electric forces which arise from the potential fall in the liquid through which the current passes. However, the electric force will tend to bring about a displacement, relatively to each other, of the positively charged fluid layer and the negatively charged particle, whereby the fluid layer follows the flow of positive electricity while the particle moves in the opposite direction. If the liquid were a perfect insulator, the new position would still be a condition of equilibrium. Since, however, through the displacement of the layers the equilibrium of the galvanic tension between the solid particle and the liquid is disturbed, and on account of the conductivity of the liquid always seeks to restore itself, the original state of electrical distribution will tend to be continually reproduced and so new displacements of the particle with respect to the surrounding liquid will continually occur."

THE DIFFUSE DOUBLE LAYER

The original conception of the double layer as two arrays of oppositely-charged ions, parallel and only one molecular diameter apart, cannot be reconciled with the kinetic theory of heat. Further, the mutual influence of electrically charged particles such as ions must be taken into account.

Gouy[2] postulated a diffuse double layer, the outer ionic layer possessing an electric density falling off according to an exponential law and its ions all participating in cataphoretic movement. Guggenheim[1] mentions that Gouy's treatment of the configuration of the double layer accepts the solvent as a continuous medium with a macroscopic dielectric constant. Thus, in his model the ions are analogous to the plates of a condenser and the solvent is analogous to a dielectric. According to Ham and Dean[2] the Gouy theory demands far too rapid a decrease in the thickness of the double layer as electrolyte concentration increases.[3]

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[1] *Vide* Briggs, *J. Phys. Chem.*, **32**, 641 (1928), and Freundlich, " Kapillarchemie " (Leipzig, 1930), Vol. I., 338.

[2] *Compt. rend.*, **149**, 654 (1909) ; *J. de Phys.*, **9**, 457 (1910) ; *Ann. phys.*, **7**, 129 (1917). See also Freundlich, *loc. cit.*, p. 356 ; Rice, *J. Phys. Chem.*, **30**, 1348 (1926) ; Porter, *Trans.*

Stern[4] resolves Gouy's double layer into a rigid (Langmuir-type) monomolecular layer and a diffuse outer layer. As pointed out by Kruyt and Overbeek[5]: "although in many cases, colloid chemistry is more interested in the potential of the double layer than in its charge, a full knowledge of the structure of the double layer requires a knowledge of the charge as well. The theory of Stern owes its existence to the fact that neither Helmholtz' nor Gouy's theory could account for the capacity of the double layer on mercury."

The essential difference between Gouy and Stern theories is that the former regarded all of the double layer ions (excepting the fixed inner sheath) as mobile with respect to hydrostatic forces, while Stern regarded both sheets of ions constituting the double layer to be immobile with respect to hydrostatic forces.[6] For extremely small concentrations of electrolyte the two theories practically coincide.[7]

An extension of the Gouy theory due to Janssen[8] assumes that the mobility of the liquid in the vicinity of the boundary is lowered because of solvation (attraction and orientation of water molecules), a layer of liquid being attached to the boundary.

THE CONCEPTION OF IONIC ATMOSPHERE

The newer views in the field of research on the dissociation of electrolytes in solution bear on the constitution of the electrical double layer.

Excellent introductions to the work of Debye and Hückel[9] are provided by various authors[10] in "A Symposium on Electrolytes"; especially interesting is the first paper by Scatchard on "The Coming of Age of the Interionic Attraction Theory."

The time-honoured theory of Arrhenius[11] held that solutions of

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Faraday Soc., **16**, Appendix, 135 (1921); Müller, *Kolloidchem. Beihefte*, **26**, 277 (1928); Mooney, *J. Phys. Chem.*, **35**, 331 (1931); Janssen, *Physik. Z. Sowjetunion*, **4**, 322 (1933).

[1] *Trans. Faraday Soc.*, **36**, 142 (1940).

[2] *Ibid.*, **36**, 57 (1940).

[3] See also Hauser and Hirshon, *J. Phys. Chem.*, **43**, 1015 (1939); Lens, *Proc. Roy. Soc.*, **A.**, **139**, 596 (1933).

[4] *Z. Elektrochem.*, **30**, 508 (1924). *Vide* Buzágh, *Kolloid-Z.*, **52**, 57 (1930); Urbanand White, *J. Phys. Chem.*, **36**, 3157 (1932); **37**, 399 (1933); Urban, White and Strassner, *Colloid Symposium Monograph* **XI**, 179 (1935); *J. Phys. Chem.*, **39**, 11 (1935); Rabinovich, *Physik. Z. Sowjetunion*, **4**, 304 (1933); Esin and Markov, *Acta Physicochim. U.R.S.S.*, **10**, 353 (1939); Voet, *Kolloid-Z.*, **79**, 15 (1937).

[5] *Trans. Faraday Soc.*, **36**, 115 (1940).

[6] Verwey, *Chem. Reviews*, **16**, 367 (1935); Grahame, *J. Am. Chem. Soc.*, **63**, 1207 (1941).

[7] Verwey, *loc. cit.*, p. 368.

[8] *Physik. Z. Sowjetunion*, **4**, 322 (1933). See also Verwey and Niessen, *Phil. Mag.*, **28**, 435 (1939).

[9] *Physik. Z.*, **24**, 185 (1923).

[10] *Chem. Reviews*, **13**, No. 1 (1933).

[11] *Z. Physik. Chem.*, **1**, 631 (1887).

electrolytes contained ions without the necessity of an external electrical force such ions being quite independent of each other and behaving as ideal solutes. The undissociated molecules contain two or more ions in so strong union as to behave as single ideal solute molecules.

Since between ions strong electrostatic fields exist, the independence of ions has been challenged [1] and the original conception of partial ionic dissociation replaced by that of complete dissociation, denying the existence of un-ionised molecules of an electrolyte. Debye and Hückel showed that an ion in a solution must be accompanied by an oppositely charged "ion atmosphere." Their simplified equation states that the potential (ψ) around a given ion is

$$\psi = \frac{\epsilon^{e-K(a-r)}}{Dr(1-Ka)},$$

where ϵ = the charge on the ion,
a = distance between the ions when their approach is closest,
r = distance from the centre of the ion,
D = dielectric constant,
K = a function of the number of ions per c.c., the Boltzmann constant and the absolute temperature.

The 'ion atmosphere' is the balanced result of the characteristic forces (attractions and repulsions) tending to ordered array of the ions, and the thermal vibrations acting against such regulation.

Applying an external electric field institutes ionic motion towards the electrodes. Retarding this motion [2] are effects due to (*a*) the ion shifts from the centre of its ionic atmosphere, there being a 'time of relaxation' effect [3] before the ionic atmosphere adjusts itself to such motion and restores the symmetry of the electrical forces, (*b*) an 'electrophoretic effect' arises from the counter-current of solvent,[4] the ion moving through a medium of opposite charge. Such ideas explain why the equivalent conductivity decreases with increasing concentration.

Burton [5] has admirably summarised the work of Gouy and Debye. He points out that their formulæ and results reveal two important properties of the Helmholtz double layer: (1) as the concentration of electrolyte increases, the thickness of the outer double layer decreases, *i.e.*, the addition of electrolytes to the liquid depresses the outer layer nearer to the inner layer; (2) ions of high valency exert a more marked depressing effect in the thickness of the outer Helmholtz layer than do ions of less valency. A third point brought out by Gouy and specially emphasised by Burton is "that if the cations have the same valencies, their concentrations remain throughout proportional to one another, and so for the anions; if the ions differ in valency, they are more concentrated or rarefied in the neighbourhood of the surface depending on the valency."

The Gouy-Debye view, then, of a charged particle is that the effective charge on the surface is not neutralised by the outer Helmholtz ionic layer until a distance is traversed and a region reached where the distribution of anions and cations is that obtaining in the main bulk of the liquid medium.

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[1] *Chem. Reviews*, **13**, No. 1 (1933), especially the paper by Scatchard.

[2] Debye, *Trans. Faraday Soc.*, **23**, 334 (1927); Onsager, *ibid.*, **23**, 341 (1927), and *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

[3] See Falkenhagen, "Electrolyte" (Leipzig, 1932), 175.

[4] Falkenhagen, *loc. cit.*, p. 178.

[5] *Colloid Symposium Monograph*, **4**, 135 (1926).

ELECTROKINETIC POTENTIAL

Freundlich[1] has especially emphasised the distinction between two electrical potentials : (*a*) Nernst's thermodynamic potential ϵ, the potential of a single electrode in a galvanic cell, and (*b*) the electrokinetic potential ζ, governing electrification at interfaces. Whilst the thermodynamical potential is measured vertically to an interface, the electrokinetic potential is measured tangentially to the interface. The latter potential is concerned in the electrokinetic phenomena already outlined.[1]

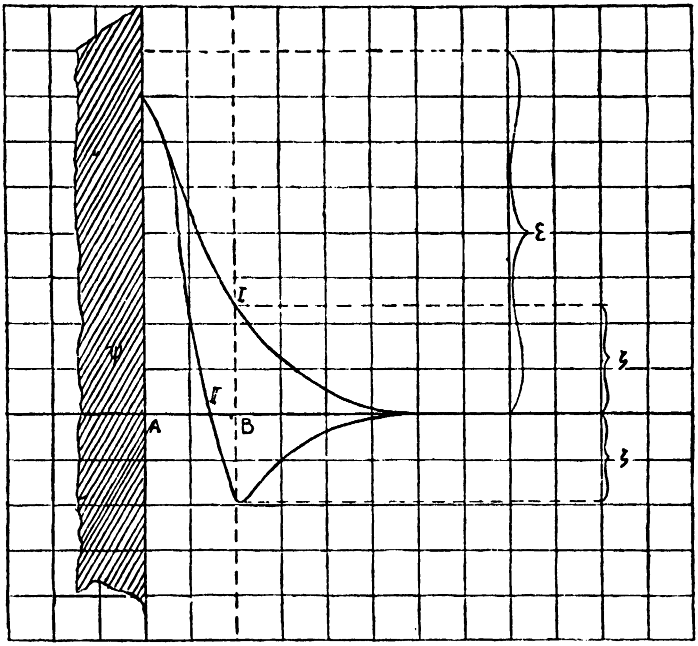

Fig. 14.—Freundlich's representation of the relation between the thermodynamic potential and the electrokinetic potential.

The distinction between ϵ and ζ rests on the conception of the electrical double layer being diffuse, so that whilst ϵ is the true potential between two phases, ζ is the potential difference between the movable liquid phase and the thin film of liquid adhering to the boundary.

Fig. 14 given by Freundlich depicts the difference in graph form. The ordinates refer to potential difference ψ, the abscissæ to the distance from the boundary between the phases. The shaded portion to the left of A represents one phase (*e.g.*, a solid wall or an oil globule), whilst between A and B is the thin film of liquid adhering to the boundary. Graphs 1 and 2 illustrate two possibilities of the change in the potential with distance from the boundary. It is clear that the value of ϵ does not depend on the value of ζ, and it may even have the opposite sign.

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[1] *Trans. Faraday Soc.*, **22**, 440 (1926) ; " Colloid and Capillary Chemistry " (London : 1926), p. 250. The theory of the zeta potential is dealt with by : March, *Trans. Faraday Soc.*, **31**, 1468 (1935) ; Bull, *J. Phys. Chem.*, **39**, 577 (1935) ; Mueller, *ibid.*, **39**, 743 (1935) ; Horwitz, *J. Chem. Education*, **16**, 519 (1939), a review with 45 refs. Methods of investigating the zeta potential are described by : Ghosh and Roy, *J. Indian Chem. Soc.*, **16**, 634 (1939) ; Lauffer and Gortner, *J. Phys. Chem.*, **42**, 641 (1938) and **43**, 721 (1939) ; Du Bois and Roberts, *ibid.*, **40**, 543 (1936) ; Monaghan, White and Urban, *ibid.*, **39**, 585 (1935) ; Bull and Moyer, *ibid.*, **40**, 9 (1936) ; Abramson, *ibid.*, **39**, 749 (1935) ; Jack and Dahle, *J. Dairy Sci.*, **20**, 551 ; 605 (1937) ; Abramson and Moyer, *J. Gen. Physiol.*, **21**, 729 (1938).

Accepting Stern's theory of the double layer (a monomolecular film adhering to the boundary), the curves would depict a *linear* fall through the distance A to B.

The coagulation of hydrophobic sols, such as two-phase oil emulsions, is closely related to ζ, and is thus greatly influenced by the valency and extent of adsorption of ions of sign opposite to that on the particles or globules. Referring again to Fig. 14, the course of the graphs 1 and 2 in the boundary region A–B must depend on the number and the valency of the ions present in the liquid. With pure water, therefore, the potential gradient would be very gradual.

Remarkable attention has been given to the electrokinetic potential in recent years and discussion is still vigorous. The modern position is seen in two recent statements. Hartley and Roe [1] state that we can identify the ζ-potential with the potential in the vicinity of a simple ion when as near as possible to another, as considered in the Debye-Hückel theory. "We are familiar with the latter potential determining the average concentration of other ions at the distance considered. The influence of this ionic redistribution on observable properties is usually evaluated through its influence on the potential causing it. It is legitimate, and in some cases simpler, to consider the influence of this redistrition directly. Nevertheless, the fact, that the ζ-potential determines the local ionic concentrations near the surface of the particle, seems generally to have been overlooked by experimental workers."

Eilers and Korff [2] define the ζ-potential as the energy required to transfer an electron from the outer phase of the double layer to the plane where a shift takes place in case of electrophoresis.

ELECTROKINETIC POTENTIAL AND STABILITY

Fundamental in the study of hydrophobic colloids is the significance to be given to the ζ-potential.

Donnan's Liverpool school figures prominently in the early work, investigating the elementary assumption that the electrical double layer prevented coagulation of the dispersed particles so far as their kinetic energy remained ineffective in driving them through the layer. Collision is opposed by an electrical repulsion. The aim, therefore, was to investigate what connection existed between the drop in ζ-potential and the stability, using oil hydrosols. It was from this work that the idea of a critical potential originated (see p. 101).

March [3] has dealt with the adsorption theory of the electrokinetic potential. This is usually related to the potential value on the boundary :

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[1] *Trans. Faraday Soc.*, **36**, 101 (1940).
[2] *Ibid.*, **36**, 230 (1940).
[3] *Ibid.*, **31**, 1468 (1935).

free liquid/liquid adhering to the particle surface. Since the particle always retains adhering liquid, it can only react upon any influence with the ζ-potential, while the whole or ϵ-potential, representing a property of the actual surface itself, is " doomed to inefficiency." In conformity with this is the usual observation that addition of electrolyte reduces the value of ζ. However, contrary instances are known and, further, increasing concentrations of electrolytes frequently invert the sign of ζ, which is inexplicable on the assumption that the added electrolyte effects a concentration of the ionic atmosphere into the region between the particle and the boundary.

Another difficulty concerns the structure of the boundary referred to, since the adhering liquid is likely to be separated from the free liquid by a transition film several molecular layers deep and ζ may only be precisely defined if the potential does not vary appreciably within the transition film.

" There is apparently only one way to overcome these difficulties resulting from the interpretation of ζ as a part of ϵ : the assumption that the two potential differences ζ and ϵ are independent of each other and have quite different origins. On approaching the surface of the particle the potential ϕ first goes up, for some reason or other, to the value ζ and beyond that, for some other reason, to ϵ, so that the total potential difference ϵ is composed of two parts, ζ and ϵ-ζ, which have nothing to do with each other."

The primary question now is : what is the origin of the ζ-potential ? March examines two possibilities.

Admitting that the potential is due to some force (acting on the surface of the particle) which separates the ions of the surrounding electrolyte or even two similar particles, such forces can only be : (1) that which splits up the molecules of an electrolyte to yield ions, or (2) an unequal adsorption of ions by the surface of the particle. Neither view is satisfactory if a common origin of the ζ- and ϵ-potentials is assumed. Although the adsorption theory can explain potential differences of the order of ζ, it cannot suffice to explain potentials of the order of ϵ. This objection, however, is of no significance when the viewpoint is adopted that ζ and ϵ are independent quantities separately to be interpreted.

March's detailed exposition then deals with the course of the potential within a double layer due to an unequal adsorption of the ions, and the result is a very simple connection between the value ϕ, to which the potential rises in the layer, and the difference of the adsorption potentials.

Discussing March's theory [1] of a protective aqueous 'skin' around dispersed particles as the cause of stability in colloidal suspensions, Mueller [2] will only accept the suggestion if the origin and nature of the skin are understood. It is necessary to prove that the energy necessary for destruction of the skin exceeds the energy associated with the thermal motion of the particles. Also, a close connection must be found between the existence of the skin and the electrokinetic potential, whereby its influence disappears with small ζ-potentials.

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[1] *Ann. Physik.*, **84**, 605 (1927).

[2] *Colloid Symposium Monograph*, **11**, 271 (1935).

Mueller proposed an explanation of the origin of the protective skin.[1] He writes: "The electric double layer creates a very strong inhomogeneous electric field around each particle. This field produces by electrostriction a large hydrostatic pressure in the range of the double layer. We find, therefore, around each particle a thin shell where the water is under considerable pressure. It is this shell which acts as the protecting skin. According to this theory the mechanism which produces the stability of colloids is very similar for hydrophilic and hydrophobic sols. The difference lies in the fact that in hydrophilic colloids the water molecules are 'attached' to the surface of the micelle by chemical (adsorption) forces and hence coagulation is to a large degree independent of the ζ-potential. In hydrophobic colloids the water molecules are only "attracted" to the surface by the electrostatic forces of the double layer, and hence their stabilising influence diminishes as the ζ-potential gets smaller."

An equation [2] is deduced connecting the free energy (U) of water (compressed layer on the surface of the colloidal particle) with the electrokinetic potential, where U is proportional to ζ^2. Hence, whilst the thermal motion of the particles is insufficient to destroy the skin, the stability of the colloid is very sensitive to small changes of ζ.

CATAPHORESIS

A number of important investigations [3] have concerned the cataphoretic migration of oil globules in oil hydrosols. Recently, the theory of the phenomenon has been reconsidered in the light of the newer views on the ionic atmosphere.

Smoluchowski's equation for rigid electrically insulating particles of any shape (see p. 85) was derived on the assumptions: (1) due to distortion of the electric field by the presence of the spherical particle, the passage of the electric current is tangential to the surface of the sphere; (2) very thin Helmholtz double layer causes the electric field to lie parallel to this layer over its full range, and the double layer is not deformed.

Debye and Hückel [4] argued that independent of the thickness of the double layer, the Smoluchowski equation is always valid as a type, but the constant is not invariably $\frac{1}{4\pi}$, but varies with the shape of the particle. Henry [5] re-examined the argument and developed equations for the cataphoretic mobility of rigid spheres and cylinders of any desired electrical conductivity. He deduced that, provided the radius of curvature of the particle is large compared with the effective thickness of the electrical double layer, the cataphoretic mobility of an insulating particle is that given by Smoluchowski's equation. However, when the particles (as in colloidal solutions) are of size small compared with the effective thickness of the double layer, the cataphoretic mobility varies with the size, tending towards the value : $v = \frac{\zeta ED}{6\pi\eta}$ for very small particles.

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[1] *Symposia on Quantitative Biology*, **1**, 5; 60 (1933).

[2] See also Kruyt and Overbeek, *Trans. Faraday Soc.*, **36**, 116 (1940) and Eilers and Korff, *ibid.*, **36**, 241 (1940).

[3] Mooney, *Phys. Rev.*, **23**, 396 (1924); *J. Phys. Chem.*, **35**, 331 (1931); Bikerman, *Z. physik. Chem.*, **A.**, **171**, 209 (1935). A comprehensive account of the phenomenon is given by Abramson, "Electrokinetic Phenomena and Their Application to Biology and Medicine" (New York, 1934), Chapter III.

[4] *Physik. Z.*, **25**, 49 (1924); Hückel, *ibid.*, **25**, 204 (1924).

[5] *Proc. Roy. Soc.*, **A.**, **133**, 106 (1931). Cf. *Ann. Reports, Chem. Soc.*, **28**, 350 (1932). Henry's results are critically examined by Müller, *Symposia on Quantitative Biology*, **1**,

Gyemant[1] studied the influence of electrolytes on the cataphoretic mobility of water-in-oil emulsions, using guiacol and aniline. Water or solutions of inorganic electrolytes showed feeble migration, if at all. Cataphoresis is favoured by those electrolytes, which easily infiltrate into the organic solvent. In the presence of organic cations the water globules migrate to the anode, with organic anions to the cathode. Benzonitrile gave unexpected results, possibly due to impurities, *e.g.*, benzoate anions.

Kemp[2] deals with the relation between particle size and mobility. He first reviews the theory of cataphoresis[3] and then experimentally examines Henry's equation, finding this to be correct for about ±5 per cent. for insulating particles and may be relied upon to predict with this accuracy the variation of mobility with size over the range κb from 2 to 330 (where κ is the reciprocal of the thickness of the ionic atmosphere and b is the radius of the particle).

Structural influence of the particle affecting cataphoretic mobility has been investigated by Alty and Johnson[4] who employed small cylinders of paraffin, some coated with aliphatic acids and amides, in pure water and in dilute HCl. Both the length of the hydrocarbon chain and the nature of the water-soluble groups had a considerable effect on the mobility. With constant chain length the mobility decreased as the water-soluble group changed in the order : $-CONH_2$, $-COOH$ and $-CH_2OH$. With $-COOH$ as the end group the mobility decreased as the length of the chain increased. A double bond near the middle of the

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9 (1933). Related papers are : Abramson, *J. Phys. Chem.*, **35**, 289 (1931) ; Abramson and Michaelis, *J. Gen. Physiol.*, **12**, 587 (1929) ; Hacker, *Kolloid-Z.*, **62**, 37 (1933) ; Mattson, *J. Phys. Chem.*, **32**, 1532 (1928) ; Craxford, *Phil. Mag.*, **16**. 268 (1933) ; Newton, *ibid.*, **9**, 769 (1930) ; Bikerman, *Z. Elektrochem.*, **39**, 526 (1933) ; Tuorila, *Kolloidchem. Beihefte*, **24**, 1 (1927).

[1] *Z. physik. Chem.*, **102**, 74 (1922). See also *J. Phys. Chem.*, **43**, 743 (1939).

[2] *Trans. Faraday Soc.*, **31**, 1347 (1935). See also Proszt, *Roy. Hung. Palatin-Joseph Univ. Tech. Econ. Sci., Sopron. Pub. Dept. Mining Met.*, **7**, 26 (1935) who found that in the range 1 to 10μ the velocity increases directly with diameter in the case of paraffin emulsions.

[3] For theory see Bikerman, *Z. physik. Chem.*, **A.**, **171**, 209 (1935) ; Rutgers and Overbeek, *ibid.*, **A.**, **177**, 29 (1936) ; Hermans, *Phil. Mag.*, **26**, 650 (1938) ; Komagata, *Researches Electrotech. Lab. Tokyo*, **387**, 35 pp. (1935) ; White, Monaghan and Urban, *J. Phys. Chem.*, **39**, 611 (1935) ; Mueller, *Ann. N.Y. Acad. Sci.*, **34**. 111 (1939) ; the collection of papers in *Trans. Faraday Soc.*, **36**, 1—322 (1940) ; Klemm, *Physik. Z.*, **39**, 783 (1938) ; Sen-Gupta, *J. Indian Chem. Soc.*, **15**, 483 (1938) ; Longsworth, *J. Am. Chem. Soc.*, **61**, 529 (1939) ; Craxford, Gatty and McKay, *Phil. Mag.*, **23**, 1079 (1937).

[4] *Phil. Mag.*, **20**, 129 (1935). See also the recent publication by Williams on the electrophoresis of certain hydrocarbons and aliphatic esters as a function of *p*H, *Trans. Faraday Soc.*, **36**, 1042 (1940).

chain increased the mobility, while increasing H-ion concentration decreased the mobility.

INVESTIGATIONS BY LEWIS

Since 1936 a series of papers on electrophoretic mobility has appeared from the Liverpool school of Lewis. The more salient findings only can be outlined here.

Roberts[1] investigated the electrophoretic behaviour of purified tristearin dispersions, the intention being to use a reproducible 'inert' surface for comparison with the behaviour of other long chain compounds. Accurate control of *p*H was found essential with water emulsions containing 0·6 gm. of the fat. Points investigated were the effect of *p*H on the emulsions in various buffer solutions, and in the presence of NaCl and KCl, the mobility of tristearin at constant *p*H at different salt concentrations, mobility in the presence of the chlorides of the alkali metals and the mobility in the absence of added salts of buffers.

The general conclusion drawn is that the mobility is affected by added salts but that there is relatively little specific difference between the effects of salts containing cations of the same valency. The controlling factor is *p*H value. Roberts concludes, however, that the mobility is a function of the *electrokinetic charge density* which is to be regarded as the more fundamental property of the system. Calculation shows that the electrokinetic charge density (equal in magnitude and of opposite sign to the charge in the diffuse double layer) *increases* with fall in *p*H in the absence of electrolyte, but *decreases* with fall in *p*H if salt is present. At constant *p*H it increases with increasing salt concentration.

In order to account for the variation in electrokinetic charge density the assumption is made of either primary adsorption of the added anions or exchange of H^+ ion in the rigid secondary layer by the added cations, thus producing a less tightly bound system which increases the effective electrokinetic charge. Under comparable conditions as regards concentration H^+ ion is much more strongly adsorbed into the rigid secondary layer than is any other cation. Exchange, in the sense of removal of H^+ ion, is only brought about when the concentration of the added cation is much greater than that of H^+ ion. It is concluded that the amount of H^+ ion adsorbed in the rigid secondary layer is a function of the effective primary charge as well as of *p*H value.

Measurements of mobility were next made in the alkaline region.[2] Variations in the concentration of the OH′ ion are very effective upon the mobility and uniquely so, its effect being noticeable even in very low concentrations. Thus, an increase in *p*H from 2·2 to 9, corresponding to a rise in the bulk concentration of the hydroxyl ion $1{\cdot}6 \times 10^{-12}$N to 1×10^{-5}N, causes an increase in the electrophoretic mobility in 0·01 N sodium salt from 0 to $55{\cdot}7 \times 10^{-5}$ cm./sec./v./cm., but a further rise in the concentration of this ion to approximately 1×10^{-2}N raises the mobility only a further 5 units. "The inference to be drawn from this is obvious. It appears that initially, on increasing the hydroxyl ion concentration in the dispersions, this ion plays a part in the formation of the double layer system which is not available to any of the other anions which have been examined. Once this initial effect has exhausted itself, further additions of anions, whether hydroxyl or not, are accompanied by a variation in the electrophoretic mobility which is independent of the nature of the added anion."

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[1] *Trans. Faraday Soc.*, **32**, 1705 (1936).
[2] *Ibid.*, **33**, 643 (1937).

Breese and Lewis [1] studied the effect of cations on the electrophoretic mobility of tristearin at constant *p*H value (*p*H = 4) and again called attention to the increase in the electrokinetic charge density with the increase in concentration of electrolyte, a behaviour incapable of explanation by an appeal to capillary data obtained necessarily at a liquid/liquid interface.

Later, these authors [2] extended the study to include such cations as K and Li, together with the anions Cl, I and CNS. A new phenomenon of special theoretical significance was observed with anions. Whilst previous results showed that NO_3 and Cl ions are indistinguishable in their influence, potassium and especially lithium salts, iodides and thiocyanates, caused the mobility at first to fall, then pass through a flat minimum and then to rise steadily with increase in the concentration of the salt. This increase in mobility which occurs in the region of relatively high concentration is to be distinguished from the long familiar initial rise in mobility exhibited at very low concentrations of univalent electrolytes. "The simplest explanation is that iodide and thiocyanate ions possess the property of being primarily adsorbed upon the tristearin surface, thereby increasing the negative charge density upon that surface with consequent increase in electrokinetic potential, and therefore in mobility. This property is apparently possessed by chloride ion to a much less extent, and may, in fact, be entirely absent. The initial lowering in mobility is to be attributed to the cation, this being the normal behaviour." That the effect thus mentioned is due to primary adsorption of iodide and thiocyanate ions upon the fat is supported by observations of the capillary behaviour of these ions at hexane/water and decalin/water interfaces, and by the work of Dickinson.[3] This author reported on the effect of certain potassium salts on the electrophoretic mobility of cetyl acetate emulsions and on the interfacial tension between cetyl acetate and water.

Growney [4] investigated the electrophoretic mobilities of esters containing various amounts of stearic acid in the presence of 0·01 N sodium ion over the *p*H range 2 to 12. He compared also the mobility-*p*H curves of the two separate components with those of the complex globules. It was found that the mobilities for the complex systems do not lie in an intermediate position with respect to the mobilities of the two constituents alone. The inference is that the orientation of the surface layer of the stearic acid in the complex globule differs from that which occurs in the case of particles of the acid itself.

[1] *Trans. Faraday Soc.*, **34**, 787 (1938).
[2] *Ibid.*, **34**, 1515 (1938).
[3] *Ibid.*, **36**, 839 (1940).
[4] *Ibid.*, **37**, 148 (1941). See discussion on this paper, p. 191 *et seq.*

Another contribution from Lewis' laboratory[1] concerned electrophoretic mobility measurements in an attempt to determine the effect on the mobility of introducing a double bond and certain groups into a saturated hydrocarbon, in the presence of 0·01 N sodium ion over the *p*H range 2 to 12. It was found that an increase in chain length had no effect on the mobility of a saturated hydrocarbon if no change of state took place and the conclusion was drawn that the mobility effect of the end group could be related to the "residual charge" associated with it. The residual charge, which arises from the unequal sharing of electrons between the group concerned, and the rest of the molecule, results in a net charge on the end group, which attracts or repels hydroxyl ions to the adsorption layer according to its sign. Thus, if the end group is associated with a net negative charge, hydroxyl ions are assumed to be repelled from the adsorption layer, reducing the negative charge at the interface. Accordingly, the mobility of emulsions of the appropriate compound is less than the mobility of emulsions of a compound whose end group is characterised by a zero residual charge.

Dickinson[2] extended this investigation to the effect of *p*H on the electrophoretic mobility of emulsions of the hydrocarbons octadecane and paraffin wax and the aliphatic halides cetyl and octyl iodides, cetyl bromide, and cetyl, octadecyl, and lauryl chlorides. It was found that always the emulsions carry a small positive charge in the lowest *p*H values, but with increase in *p*H the charge is reversed while the *p*H is still small. Further increasing the *p*H leads to increased negative charge, to attain an almost constant value above *p*H = 9. The full report should be consulted for the discussion on the source of the negative charge on the particles in relation to the effect of *p*H on the charge and for further remarks dealing with the residual charge on the end-group.

Dealing with the electrophoresis of certain hydrocarbons and their simple derivatives as a function of *p*H, Carruthers[3] ascribed the difference in mobility produced by the change of state from solid to liquid to the difference in surface densities of the molecules produced by the change of state. He deduced numerical values for the mobility effects produced by the introduction of various groups into the end of a paraffin and discussed the relation of these values to the residual charges on the end groups.

Assuming that the formation of interfacial films concerns both electrophoretic mobility and interfacial tension, some qualitative agreement between the two data might be expected. Powney and Wood,[4] however, noted anomalies when certain paraffin chain salt solutions were examined. Particularly was this the case at lower concentrations where there is often a high mobility maximum accompanying inappreciable interfacial activity. Such high mobilities can only arise from the influence of the long chain ions. The location and orientation of such ions at the oil/water interface are no doubt the factors operating. The interface :

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[1] Carruthers, *ibid.*, **34**, 300 (1938).
[2] *Trans. Faraday Soc.*, **37**, 140 (1941).
[3] *Ibid.*, **34**, 300 (1938).
[4] *Ibid.*, **37**, 152 (1941).

oil/dodecyl pyridinium iodide solution provided the most outstanding anomaly.

The authors report that: "Whilst the mobility of Nujol in water is $-4{\cdot}35$ μ/sec./volt/cm. at 25°, the addition of only 0·000075 % $C_{12}H_{25}.C_5H_5N.I$ reduces the mobility to zero and on further increasing the concentration to 0·0004 % the mobility attains a maximum value of $+5.8$. Similar changes in mobility have also been observed in $C_{12}H_{25}.C_5H_5N.Cl$ solutions. Lowering of interfacial tension, on the other hand, is quite inappreciable at concentrations below 0·01 % and it is only when the critical concentration (approximately 0·4%) is reached that the mobility and interfacial tension data show any correlation. The high positive mobility shown at extremely low concentrations can only be due to the dodecyl pyridinium cations and the question arises as to whether these long chains will be situated actually in the oil-water interface, a process which might be favoured by the strong electrostatic attraction, or be present as an atmosphere in proximity to the interface. If there is definite adsorption, then it is difficult to understand why there should be no measurable interfacial activity even at concentrations twenty times higher than those at which high positive mobilities are attained. On the other hand, if there is no adsorbed film in the normal sense of the term, it is difficult to reconcile the incomparably greater sensitivity of the mobility of Nujol towards $C_{12}H_{25}C_5H_5N.I$ than towards a simple uni-univalent electrolyte such as NaCl."

THE STABILITY OF EMULSIONS

We have already noted that *concentrated* emulsions demand the presence of an emulsifying agent. In such cases the stability of the emulsion depends on factors chiefly relating to an adsorbed film at the oil/water interface.[1] This subject is discussed later (p. 199).

For emulsions of oil in pure water the stability is influenced by (*a*) the interfacial tension, tending to bring about coalescence of the globules, whereby the total surface would be reduced ; (*b*) the Brownian movement, tending to collision of the globules, a factor against stability ; and (*c*) the electric charge on the globules, tending to repel them on near approach.

For two-phase emulsions, such as were studied by Lewis,[2] Ellis, Powis and Hatschek, the interfacial tension between the oil and water is of the order of 48 dynes/cm. Pockels [3] found the value of 48·3 dynes/cm. for the interfacial tension between water and a petroleum oil. Measurements by Limburg [4] showed that the interfacial tension: paraffin oil/water decreased very slightly with KCl up to 0·09 N, increased very slightly with HCl up to 0·1325 N, but decreased considerably in the presence of K_2CO_3.

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[1] See the interesting papers by Nasini and Balian, *Atti X° congr. intern. chim.*, **2**, 365 (1938) on "Electrophoretic Mobility and the Protective Action of Emulsifying Agents"; Martin and Hermann, *Trans. Faraday Soc.*, **37**, 30 (1941) on "Partial Coagulation of a Standard Emulsion in Sodium Oleate Solution by Salts of some Bi- and Highervalent metals."

[2] *Phil. Mag.* (1908), p. 509.

[3] *Wied. Ann.*, **67**, 668 (1899).

[4] *Rec. trav. chim. Pays-Bas.*, **45**, 861 (1926).

Using a pure paraffin emulsion containing 89 mg. oil per litre, Limburg determined the cataphoretic velocities at 25° C. under the influence of various electrolytes. His results are indicated in Fig. 15, from his paper.

Influence of Monovalent Cations. With increasing concentrations of KCl, K_2CO_3, and HCl the cataphoretic velocity increases to a maximum and then falls off (the maximum was not reached for K_2CO_3). At the low concentrations of electrolytes, the anion is more strongly adsorbed than the cation. As the electrolyte concentration is increased, the cation adsorption becomes more and more pronounced.

Influence of Polyvalent Cations. In the case of $BaCl_2$ at low concentrations there is very little change, but as the concentration increases, the anion is more strongly adsorbed than the cation. With $AlCl_3$ or $Th(NO_3)_4$ as electrolyte, the cataphoretic velocity at first decreases, then becomes *nil*, and then changes in sign. It may be that the products of hydrolysis of these salts concentrate at the oil/water interface, conferring a positive charge on the oil globules ; alternatively, a strong adsorption of cations is indicated.

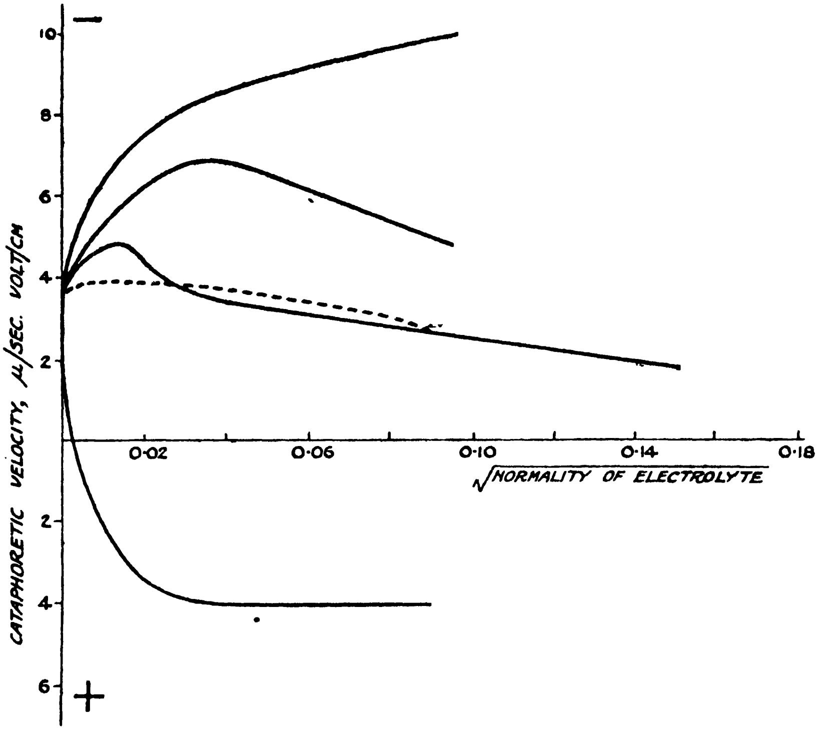

FIG. 15.—Influence of electrolytes on the cataphoretic velocity of oil globules (Limburg).

The effect of added salts on oil hydrosols is, of course, a special instance of the general problem of the coagulation of colloidal solutions.[1] The kinetics of this coagulation have been examined by Smoluchowski [2] who distinguished a zone of *slow* coagulation (small amounts of added electrolyte effecting a pronounced decrease in the time required for coagulation) and a zone of *rapid* coagulation (further addition of electrolyte causing precipitation). There is evidence that the coagulation of dilute oil emulsions (by mercuric chloride), as measured by viscosity, is not continuous with coagulation time in the slow region and that the occurrence of breaks or discontinuities tends to be more pronounced the lower the concentration of the electrolyte.[1] The nature of the 'oil' dispersed in the water may complicate the problem, as was observed by Bolam and Duncan [2] in their studies on ionic interchange in stearic acid hydrosols. The surface molecules of the particles dissociated in the manner of a weak acid and the hydrogen ions so produced led to interchange with the added salt cations. Thus, the coagulating by a salt under these conditions was closely related with the tendency of the cation to displace hydrogen ion from the surface of the particles.[3]

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[1] See, for instance, Weiser : " Colloid Chemistry " (New York : 1939), Chapter XVI.

[2] *Physik. Z.*, **17**, 587 (1916) ; *Z. physik. Chem.*, **92**, 129 (1917).

Most of the work on emulsion stability relates to the influence of added electrolytes. Hardy [4] suggested that, when colloid suspensions are coagulated under the influence of electrolytes, the particles adsorb oppositely-charged ions so that their charges become neutralised, and at the iso-electric point, where the potential difference between the particles and the medium becomes zero, stability is least. Coagulation occurs over a *range* whose magnitude depends on the extent of the coagulating factors. Bredig [5] correlated Hardy's view with the Lippmann effect (connecting surface tension and potential difference), and proposed a theory of colloid coagulation as follows: The interfacial tension between colloid particles and their medium acts in such a way that any increase in this tension tends to bring about a decrease in the surface exposed, *i.e.*, by coagulation of the particles. Now the interfacial tension between mercury and an electrolytic solution is a maximum when the potential difference between the two phases is zero. Hence, if the value of ζ between colloid particles and their medium be decreased, as by the adsorption of oppositely-charged ions from added electrolytes, the stability is weakened with resulting coalescence.

Ellis,[6] however, showed that Bredig's theory does not hold in the case of pure oil-in-water emulsions. He found his emulsions most stable in the presence of 0·001 N. NaOH, at which concentration the contact potential was a maximum. Ellis found that the rate of coagulation of the oil globules was practically independent of the interfacial tension, depending only on the electrical potential at the surface of the globules. On adding HCl to an oil-in-water emulsion, the interfacial tension did not vary within the limits of experimental error, whilst the stability decreased enormously as the acid was added. Ellis collected his data *re* the effect of acid and alkali on the interfacial tension, the interfacial potential difference, and the radius of the globules, in the graphs reproduced in Fig. 16.

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[1] Joshi and Sarkar, *J. Univ. Bombay*, **4**, 140 (1935).

[2] *J. Chem. Soc.*, **1936**, 1317.

[3] Cf. Martin and Hermann, *Trans. Faraday Soc.*, **37**, 37 (1941).

[4] *J. Physiol.*, **24**, 288–304 (1899); *Z. physik. Chem.*, **33**, 385 (1900); *Nature*, **109**, 226 (1921).

[5] "Anorganische Fermente" (Leipzig), 1901.

[6] *Trans. Faraday Soc.*, **9**, 14 (1913); cf. Donnan, *Report of British Assocn.* (Liverpool, 1923), 75–78.

Powis[1] studied the effect of KCl, $BaCl_2$, $AlCl_3$, and $ThCl_4$ on the value of ζ at the interface between oil and water in emulsions of cylinder oil in water. For the pure emulsion ζ was 0·046 volt, the sign being negative. When KCl was added, the negative potential was raised at first, but with greater amounts of KCl it was depressed. A similar maximum was found by Ellis for NaOH. If $BaCl_2$ be added to the pure emulsion ζ is altered in sign, assuming a small positive value. With $AlCl_3$ ζ becomes positive, and then remains constant over a wide range of concentrations, whilst with $ThCl_4$ ζ becomes positive, passing through a maximum and then decreasing, still retaining the positive sign.

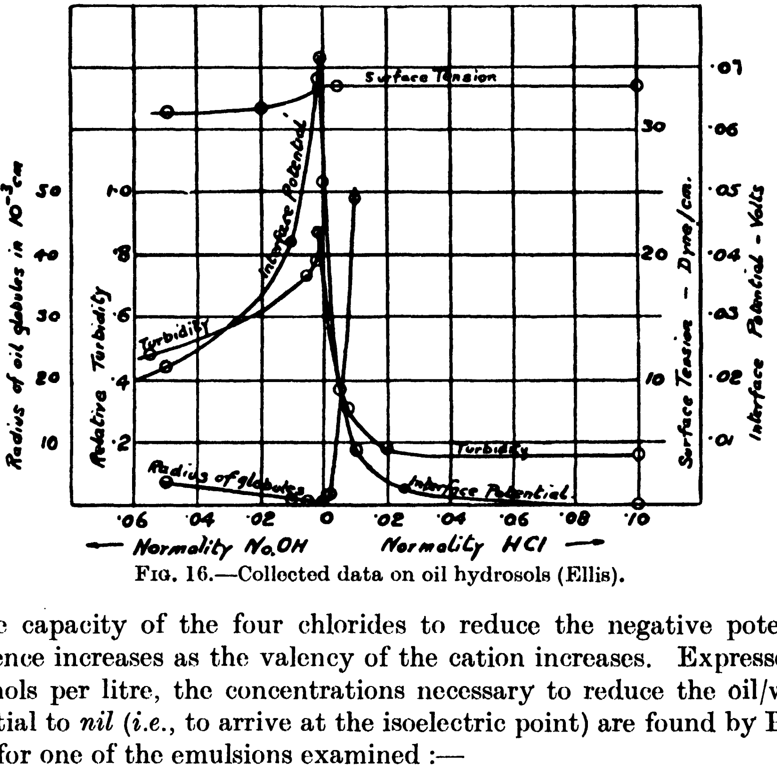

FIG. 16.—Collected data on oil hydrosols (Ellis).

The capacity of the four chlorides to reduce the negative potential difference increases as the valency of the cation increases. Expressed in millimols per litre, the concentrations necessary to reduce the oil/water potential to *nil* (*i.e.*, to arrive at the isoelectric point) are found by Powis to be for one of the emulsions examined :—

KCl	about 5,000
$BaCl_2$	95
$AlCl_3$	0·51
$ThCl_4$	0·0156

His results show that all anions strive to make ζ more negative, and all cations to make it more positive, the actual effect being the result of both actions. Powis correlates his results with the views of Freundlich[2] that the effect of added electrolyte on ζ at the surface of a particle is due to the preferential adsorption of anions or cations. If the cation is more strongly adsorbed, the value of ζ falls; in the opposite case it rises. The smaller the concentration of the oil globules, the smaller is the electrolyte concentration necessary to attain a given potential.

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[1] *Z. physik. Chem.*, **89**, 91 (1914).
[2] *Ibid.*, **73**, 385 (1910).

Later, Powis[1] carried out measurements on oil/water emulsions to which small amounts of the four chlorides were again added. He obtained the very important result that, when the oil/water potential difference reaches a definite *critical* value of approximately 0·030 volt (+ or −), the emulsion is relatively stable. Should ζ be smaller, coagulation follows with a velocity which is approximately the same for all values of ζ.

This behaviour contradicts the previously accepted view that the stability decreases continuously with ζ and that at the zero point (iso-electric point) coagulation occurs. Similar results were obtained by Powis[2] with arsenic sulphide hydrosol.

The same worker[3] in a further paper deals with the influence of time on ζ at the surface of oil globules in water. The results do not admit of simple explanation and demand further research. The value ζ of a pure oil/water emulsion remains constant for a time, then falls slowly and then little or no change follows. By the addition of electrolyte to a pure oil/water emulsion, the interface potential changes immediately, or nearly so, to a value depending on the concentration of the electrolyte. Afterwards, a further change slowly occurs until equilibrium is attained. This slow change does not appear simply as a continuation of the quicker process. In the presence of a definite amount of $BaCl_2$ the slow change proceeds to a value which would have been given originally by a higher concentration of the electrolyte. With substances like $AlCl_3$, on the contrary, the slow alteration is directed in the opposite direction, because hydrolysis replaces Al ions by hydroxide and thus ζ endeavours to change to a value corresponding to a less concentrated solution.

Abramson[4] believes that Powis' results show the existence of two stages, a rapid charging stage which is a function of the initial concentration of electrolyte and a less rapid stage which depends upon the attainment of a surface equilibrium, this being complicated when salts like $AlCl_3$ and $ThCl_4$ are present. Time changes at the interface of organic substances and water have, in fact, been demonstrated by Miss Pockels[5] repeating experiments by Devaux on wetting phenomena.

Sen[6] has estimated ζ between two phases by cataphoretic and electro-osmotic experiments. He notes that since ζ between oil and water is negative, the presence of KCl and $K_4Fe(CN)_6$ concentrates more negative ions on the oil interface, so that a greater negative charge is built up. $K_4Fe(CN)_6$ raises the negative charge more than does KCl. In the case of mixtures of KCl and $BaCl_2$ or $K_4Fe(CN)_6$ and $BaCl_2$ there is considerable antagonistic action because one of these electrolytes raises the value of ζ whilst $BaCl_2$ lowers it. When using a mixture of KCl and $K_4Fe(CN)_6$

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[1] *Ibid.*, **89**, 186 (1914).

[2] *J. Chem. Soc.*, **109**, 734 (1916).

[3] *Z. physik. Chem.*, **89**, 179 (1914).

[4] "Electrokinetic Phenomena and Their Application to Biology and Medicine" (New York, 1934), p. 230.

[5] *Kolloid-Z.*, **62**, 1 (1933).

[6] *Z. anorgan. Chem.*, **152**, 221 (1926).

only a slight antagonism results, because at certain concentrations KCl causes a decrease whilst $K_4Fe(CN)_6$ still raises the negative charge. The effect is not so pronounced as with $BaCl_2$.

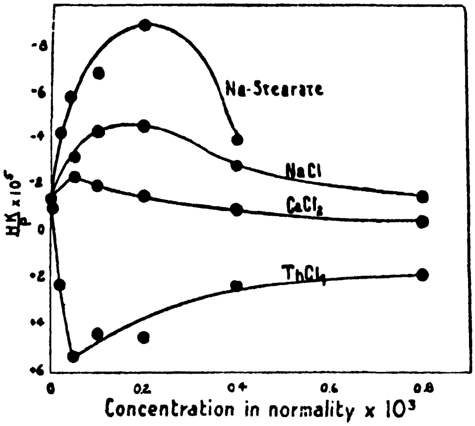

FIG. 17.—Electrokinetic potential curves for paraffin oil/aqueous solution interfaces as measured by the streaming potential (Bull and Gortner).

Using entirely different technique, Bull and Gortner[1] determined the electrokinetic potentials with solutions of NaCl, $CaCl_2$, $ThCl_4$ and Na stearate against Nujol (pure medicinal paraffin oil). Fig. 17 from their paper shows the electrokinetic potential curves for paraffin oil/aqueous solution interfaces as measured by streaming potential. The ordinates are expressed in terms of kH/P, which is directly proportional to the zeta potential, since the other factors remain constant in the experiments. Their full equation is :—

$$\zeta = \frac{4\pi\eta kH}{P\epsilon},$$

where : ζ = the potential at the interface,
η = coefficient of viscosity of the aqueous solution,
k = specific conductivity of the aqueous solution,
H = observed E.M.F.
P = hydrostatic pressure of the streaming aqueous solution,
ϵ = dielectric constant of the aqueous solution.

All the values are expressed in electrostatic units.

The authors point out that their measurements concern only a part of the true zeta potential owing to their method. The high increase of the potential attributed to the presence of Na stearate is explained on the basis that the negative stearate ion becomes adsorbed in the oil layer and imparts a high negative charge to the oil side of the interface.

THE CRITICAL POTENTIAL

The investigations of Powis have aroused continued discussion ; opinion has been divided regarding the validity of a critical potential zone in coagulation.

Limburg[2] rejects the idea of a critical potential, and his experiments with very dilute paraffin emulsions are called in support. Mukherjee and Raichourdhuri[3] also do not accept the view that a critical potential is involved in the coagulation of colloids. However, Kruyt[4] and his co-workers, studying the rate of cataphoresis of arsenious sulphide hydrosol in the presence of KCl, come to the conclusion that there is no justification for rejecting the theory of critical potentials. Rideal[1] shows that electrostatic attraction may occur between colloid globules or particles at the iso-electric point, assuming the electric double layer is to some extent movable over the surface of the particles. Postulating a mobile double layer, electrostatic attraction of globules is possible owing to the displacement effect, even when the total net charge is not zero, just as Powis found.

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[1] *Proc. Nat. Acad. Sci.*, **17**, 288 (1931).
[2] *Rec. trav. chim.*, **45**, 772, 854, 875 (1926).
[3] *Nature*, **122**, 960 (1928).
[4] *Colloid Symposium Monograph*, **4**, 304 (1926) ; *Z. physik. Chem.*, **A.**, **167**, 312 (1933).

Coagulation occurs in general when an increase of the electrolyte concentration reduces the zeta potential through a crowding together of the diffuse ionic atmosphere in the sense of Müller's theory.[2] Rabinovich[3] points out that any promising theory of coagulation must be based on the shifting of a double layer. The charged particle is surrounded by a layer of oppositely charged ions. Those lying nearest are adsorbed and move along with the particle, the rest forming a diffusion layer. Addition of electrolyte causes a contraction of the ionic layer as a result of electrostatic forces, and at the same time an exchange adsorption in the adsorption layer. This results in a change in the zeta potential and the stability of the system.

Abramson[4] believes that it is necessary to distinguish between the critical potential of *rapid* coagulation and the critical potential of *beginning* coagulation. The latter is what Powis investigated, and it is the first value of the electrokinetic potential where the forces of attraction are overcome sufficiently to permit the formation of aggregates, complete coagulation ensuing in due time.

ADHERENCE AND COALESCENCE IN EMULSIONS

Powis[5] drew attention to the fact that in his oil hydrosols, globules could *adhere* and form clumps wherein the globules remained as individuals ; also globules could *coalesce*, thereby losing their identity. He noted that whilst adherence may be attained more or less rapidly, the subsequent stage of coalescence may be relatively slow, with the tendency to coalesce being most marked in the absence of added electrolyte.

Lewis[6] has subjected the phenomena to theoretical examination. The individual globules in clumps are considered to be separated (even when in closest contact) at certain limited areas on their surfaces by an exceedingly thin film of the aqueous continuous phase. This film contains a number of ions opposite in sign to those primarily adsorbed

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Jenny and Reitemeier, *J. Phys. Chem.*, **39,** 599 (1935) accept the conception of a critical potential as does Weiser, "Colloid Chemistry" (New York, 1939), p. 222. See also Doryagin, *Chem. Abs.*, **32,** 3233 (1938).

[1] "Surface Chemistry" (Cambridge, 1926), p. 273.

[2] *Kolloidchem. Beihefte*, **26,** 257 (1928).

[3] *Chem. Zentr.*, **1932,** 1, 365.

[4] "Electrokinetic Phenomena and Their Application to Biology and Medicine" (New York, 1934), p. 200. See also Rice, *J. Phys. Chem.*, **30,** 189 (1926).

[5] *Z. physik. Chem.*, **89,** 186 (1914).

[6] *Trans. Faraday Soc.*, **30,** 958 (1934). An important related paper is that of Briggs, *J. Phys. Chem.*, **34,** 1326 (1930). A thorough discussion of the general aspects of the coagulation of colloids is given by Wiegner, *J. Soc. Chem. Ind.*, **50,** 55 T. (1931).

upon an oil globule itself, and the film at its thinnest part consists approximately of two Helmholtz layers. The problem now is to find the condition necessary for two globules to approach sufficiently close that the van der Waals attraction forces may operate.

Brownian motion decides the approach of the globules. The simple idea that adherence occurs when $\zeta = 0$ is untenable ; the critical potential of Powis, as an electrokinetic potential difference of appreciable magnitude " below which adherence occurs more or less rapidly, raises the question of how far the *average* kinetic energy of translation of the particles is, in fact, capable of overcoming the mutual electric repulsion between two particles." Adherence is concerned with the electrokinetic charge operative in the diffuse portion of the double layer, whilst in coalescence the total charge is investigated.

Mutual respulsion is due to only a small fraction of the total electrokinetic charge, since at distances beyond the thickness of the diffuse double layer the globules are effectively uncharged. Repulsion is only manifested locally, at areas where the mutual diffuse layers intermingle. One of the limits, therefore, in the expression for the electric repulsion must be in the thickness of the double layer, and this is a function of the concentration of the electrolytes in the dispersion medium. With sufficient electrolyte this thickness reaches the limiting value of the order of a molecular diameter and $\zeta = 0$.

Lewis advances considerations which indicate that the Powis estimate of 30 millivolts for the true critical potential is too high. The subsequent change of adherence to coalescence is considered in the light of the decrease in interfacial energy over the area of adherence, and it is shown that surface energy is probably adequate to account for the removal of the water molecules which separate two adhering oil globules.

The work of Donnan's school, by Ellis, Powis, Lewis and Bhatnagar, on neutral oil emulsions, shows that there is a close similarity between such " mechanical " emulsions and colloidal suspensions. In each the particles carry an electric charge of the same order of magnitude, the limiting grain-size is similar, the potential difference values are similar, and the conditions for stability under the action of adsorbed ions are also similar. Thus the electrical factors far outweigh the effect of interfacial tension. All further work has but served to emphasise the close connection between the stability and electrokinetic behaviour of colloidal suspensions.

Ellis [1] has emphasised the subject in his paper on " A Neutral Oil Emulsion as a Model of a Suspension Colloid," which recapitulates much of his previous work.

MODERN OPINIONS ON CRITICAL POTENTIAL

A general summary of the present position of the electrical double layer and the stability of emulsions has been published by Verwey.[2]

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[1] *Trans. Faraday Soc.*, **9**, 14 (1913). See also Bhatnagar, *ibid.*, **16**, Appendix, p. 27 (1921); *J. Phys. Chem.*, **25**, 735 (1921); *Kolloid-Z.*, **50**, 48 (1930); Ghosh and Dhar, *J. Phys. Chem.*, **30**, 294 (1926); Westgren and Reitstötter, *Z. physik. Chem.*, **92**, 750 (1918); Mukherjee, *J. Chem. Soc.*, **115**, 464 (1919); **117**, 1569 (1920).

[2] *Chem. Reviews*, **16**, 388 (1935); Hydrophobic Colloids (Symposium : Utrecht, 1937), p. 58; *Trans. Faraday Soc.*, **36**, 192 (1940).

He commences with the argument that where two immiscible liquids are in contact, the potential difference between the interior of the liquids is determined by a distribution equilibrium of the ions present. Each electrolyte, distributed about two phases, acts as a potential-determining electrolyte, notwithstanding only very slight solubility in one of the phases. The electrolytes may have been added or may be adsorbed impurities at the liquid/liquid interface. The generally unequal distribution coefficient of the anions and cations at the interface causes the electrical double layer. In the bulk liquid phases there are no space charges and the ionic concentrations are constant. In the neighbourhood of the interface the ionic concentration of one sign increases and that of the other sign decreases, but the total charge on both sides of the interface is equal and of opposite sign (double layer with two diffuse layers).

Verwey discusses two types of emulsion stability: (1) *primary stability* (peptisation) which is not stability in the thermodynamic sense but refers to the stability of the emulsion towards coagulation or adhesion of the globules; (2) *secondary stability,* the stability of the existing hydrosol when electrolytes are added. He examines the distribution of the electrical potential in the neighbourhood of the dineric interface. Proceeding from one phase to the other, the potential falls off continuously on both sides of the interface because both phases are able to contain one of the ions in excess. The double layer potential is therefore divided into two parts.

The fundamental problem concerns the stability of the very dilute two-phase emulsions of "pure" oil and water and the quite stable three-phase emulsions which contain an emulsifying agent. To understand the real difference between these systems Verwey believes it is necessary to investigate: (1) the ζ-potential needed for stability under the conditions of preparation of the hydrosols (critical ζ-potential for primary stability), and (2) the nature of the electrical potential functions in the double layer.

Verwey's papers should be consulted for the detailed arguments. His summary, however, presents the main conclusions which are that the critical ζ-potential for primary stability will be of the order $\pm$ 100 mV, and higher in other media. Assuming that the double layer originates from the ionic distribution equilibrium of electrolytes in the two liquid systems, it is shown that a sufficiently high ζ-value can never be reached for the following reasons: (1) the concentration of a potential-determining electrolyte cannot be altered in one phase only, and the double layer potential is accordingly rather low; (2) the double layer has two diffuse layers, and the potential drop is divided up into two parts on both sides of the interface; the development of the electrical double layer is restricted by the dimensions of the liquid phases (size of the globules, and their mutual distances in more concentrated emulsions); all factors leading to small values of ζ and of the particle charge.

In the case of O/W hydrosols the smallest part of the double layer potential occurs in the external, aqueous phase. Even for very large values of the double layer potential (say, 0·5 volt) it is to be expected that the potential drop in the outer, diffuse, layer is less than 100 mV. With W/O oleosols the potential drop in the outer diffuse layer will be higher, but here the critical ζ-potential needed for primary stability is correspondingly higher. Moreover, the mutual hindering of the diffuse layers in the external phase will play here an important *rôle* except for very dilute emulsions.

Stabilisation of emulsions with the aid of interfacially adsorbed material,[1] including solids, is due to the liquid globules having conferred on them properties akin to those of solid particles and to the shifting again of the double layer potential drop towards the outer phase.

Several authors have re-opened the question of the critical potential.[2] In particular, Eilers and Korff[3] have severely criticised the conclusion by Powis regarding the critical potential. They cannot find any foundation for the critical potential, but believe that the factor which predominates the stability of hydrosols is the energy required to bring together two particles of the dispersion against the action of their electrical field. They derive for this energy the formula :

$$A = C\frac{\zeta^2}{\kappa}$$

where ζ = the electrokinetic potential and $\kappa = 10^{7 \cdot 364}\sqrt{\Sigma(cz^2)}$ where c = the concentration of the ion and z = the valency of the ion.

Accordingly, stability is to be interpreted as due to the electrokinetic potential and the concentration and valency of the ions in the aqueous phase. Application of the formula to the experimental data of Limburg and Powis showed satisfactory agreement. The authors emphasise the often neglected influence on the sol of rather small quantities of electrolytes which will not diminish the zeta potential, but which greatly influence the value of κ.

THE ELECTRIC CHARGE

Lewis[4] has calculated that the charge on the globules of oil hydrosols equals 4×10^{-4} electrostatic units. The equation used for this determination is based on consideration of the globule with its electrical double layer as a small condenser of two concentric spheres, whose distance apart is small as compared with the radius of the globule.

Since the size distribution of oil hydrosols lies within quite narrow limits for the majority of the globules, Lewis[5] suggests a balance between an inwardly directed capillary pressure and an outwardly directed electrostatic pressure. He has considered in some detail the process of building up the globules by accretion of uncharged oil molecules, possessing zero energy in respect of electrical charge and capillary tensions. During the process of growth the charge remains constant. Assuming the existence of an electric double layer of constant dielectric capacity, equations were deduced similar to those of Knapp (see p. 80). The charge density was shown to be independent of the size of the globule, and a polydisperse system is, therefore, possible as an equilibrium condition of the system.

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[1] See Cheesman and King, *Trans. Faraday Soc.*, **36**, 241 (1940) and the present volume, p. 208.

[2] Deryagin, *Acta Physicochim. U.R.S.S.*, **10**, 333 (1939); Levine and Dube, *Trans. Faraday Soc.*, **36**, 220 (1940); Mukherjee and Chaudhury, *Science and Culture*, **1**, 111 (1935); White and Monaghan, *J. Phys. Chem.*, **39**, 932 (1935).

[3] *Trans. Faraday Soc.*, **36**, 229 (1940).

[4] "System of Physical Chemistry," Vol. I. (1923), p. 334. Important papers on the electric charge are: Koenig, *J. Phys. Chem.*, **38**, 111, 339 (1934); Rashevsky, *J. Gen. Physiol.*, **15**, 289 (1932); Harkins, *Colloid Symposium Monograph*, **6**, 17 (1928); Keller, *Kolloid-Z.*, **44**, 324 (1928); Auerbach, *ibid.*, **43**, 114 (1927).

[5] *Trans. Faraday Soc.*, **28**, 597 (1932).

However, the original conception of the Helmholtz double layer having been replaced by the diffuse layer, it follows that whilst the charge on the actual boundary of the globule remains constant, the thickness of the diffuse layer is variable and a strict proportionality between this charge and ζ, the potential of the double layer, cannot be expected. The electric charge as ordinarily understood is not the *absolute* charge as measured by Lewis, but the *effective* charge, a necessarily lower value. Whilst, for instance, there is a critical value for ζ for flocculation of the globules by electrolytes, it is quite unconnected with with any critical absolute electric charge. In other words, ζ is the electrical factor concerned in the stability of hydrosols.

Comparing the total charge of the oil globules with the mobile charge responsible for electrophoresis, Lewis found that the latter is only a very small fraction of the total charge even under the most favourable conditions for electrophoretic movement.

Later, assuming that the energy of adhesions at an interface is a measure of the upper limit which can be ascribed to the energy of the condenser due to the Helmholtz double layer of electricity associated with the interface; Lewis[1] obtained values for the (maximum) charge density at the interface : water/organic liquid in a number of cases.

Assuming that the electrokinetic effects are due to the unbalanced electrical charges upon an interface corresponding to free mobile ions of opposite sign existing independently within the solution, McBain and Williams[2] measured the number of free electric charges on air bubbles and oil globules dispersed in water containing 0·0001 N_w cetyl sulphonic acid. A simple null-point method was devised for balancing electrophoresis of bubbles and globules against gravitational rise or fall. Table 11 is from the authors' paper.

To calculate the charges on the benzene globules neglecting the electrical drag of the free mobile ions, the electrical pull Fe_n was equated with the " gravitational " pull mg, where :

F = electrical field in e.s.u./cm.
e_n = electric charge in e.s.u.
m = mass of the globule.
g = the gravity constant.

Expressed in dynes, $mg = \frac{4}{3}\pi r^3(s-s')g$, where r is the radius of the globule, s is the density of the solution and s′ is the density of the globule.

Considering the benzene globule in Table 11 with radius = 0·0041 cm.,

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[1] *Trans. Faraday Soc.*, **33**, 708 (1937).

[2] *Colloid Symposium Monograph*, **7**, 105 (1931).

TABLE 11

BENZENE GLOBULES IN 0·0001 N_w CETYL SULPHONIC ACID SOLUTION.

110 VOLTS ; POTENTIAL GRADIENT, 0·122 ELECTROSTATIC UNITS/CM. GLOBULES TIMED OVER A DISTANCE OF 1·5 MM. RADIUS OF GLOBULES STOPPED = 0·005 CM. (OBSERVED) AND 0·0041 CM. (CALCULATED).

Time of Natural Rise in Seconds for Globules of Graduated Sizes.	Effect on applying the Electric Field.
1·5	Motion still upward
2·5	Motion still upward
3·0	Motion still upward
3·0	Motion stopped
3·5	Motion stopped
3·7	Motion stopped
4·5	Motion downward (reversed)
4·7	Motion downward (reversed)
5·0	Motion downward (reversed)

it was calculated that the number of electronic charges is $5{\cdot}9 \times 10^5$. The number of possible charges, assuming a completely dissociated monomolecular film of cetyl sulphonic acid on the globule, would be $1{\cdot}03 \times 10^{11}$. Hence, the percentage of the surface covered is only 0·0006.

Du Bois and Roberts[1] used the same null-point method and with stearic and oleic acids in water obtained data comparable with that of McBain and Williams. "For drops of the same size, stearic acid appears to carry a 25 per cent. greater charge than oleic acid. In each case the number is about 1/10,000th to 1/100,000th that possible for a complete layer of ions. This fraction indicates, therefore, the proportion of the surface covered by free (ionic) charges."

Investigating non-dissociable interfaces, tetradecane/water and tetrahydronaphthalene/water, the surprising result was observed that the number of charges per cm.^{2} is approximately the same for these inert liquids as for the fatty acids, when drops of the same size are compared.

Reversing the dispersion, so that water globules were examined suspended in hydrocarbon, potential gradients up to 33 volts/cm. failed to affect the gravitational motion. Thus, although the interface remains the same, the adsorbed ions conferring a charge on the interface and the free ions in the solution compensating this charge are all self-contained within the globule and are, therefore, not relatively displaceable in the electric field.

Investigating the variation in surface density of charge with the radius of the globule, it was found that the free electric charge per cm.^{2} is a direct function of the radius, increasing rapidly with diminishing radius.

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[1] *J. Phys. Chem.*, **35**, 3070 (1931).

Modern views [1] lead to the idea that in the absence of adsorbable ions the electric charge can result by the formation of an electric double layer by dielectric polarisation.[2] The facts of molecular orientation (see p. 47) support this view.[3] The inner layer of the double layer itself in some cases contains ions of the material constituting the dispersed phase.

The electrophoretic behaviour of lecithin leads Price and Lewis [4] to the conclusion that the charge on the particles is composed of two interdependent parts both of which are of comparable magnitude. The total charge is apparently due to (*a*) adsorption of OH ions on the surface of the fatty portions of the particles, and (*b*) ionisation of the amphoteric groups. Comparison experiments were also conducted with dispersions of tristearin, $\alpha\alpha'$–dipalmitin and β-azelao–$\alpha\alpha'$–distearin. *i.e.*, fats similar to the fatty residue of lecithin, but not containing an amphoteric grouping. In the case of β–azelao–$\alpha\alpha'$–distearin, however, there is a free, ionisable COOH group.[5]

It was noted that the presence of the amphoteric grouping profoundly affects the adsorption charge of a lecithin dispersion, since (1) it lowers the initial value of the charge on the dispersion, and (2) it effectively decreases the rate of discharge by H ions to values even below those obtaining if the negative charge due to ionisation were entirely absent.

In a later communication,[6] the authors attempted to determine quantitatively the contribution from each of the two sources of electric charge already mentioned. They found that the adsorption charge passes through a minimum at the iso-electric point of the amphoteric groupings. Since the total number of negative ions adsorbed on the fatty surface was assumed to remain constant, the minimum in the adsorption charge is taken to indicate that the number of these negative ions which are effective for electrophoresis is a minimum at the point referred to.

In connection with these findings, reference must be made to the work of North and Sommer [7] on the electrokinetic potential at the fat/serum interface in milk. Here, adsorbed protein material around the fat globules has to be taken into account. The potential at the interface is the net result of adsorbed ions and the special properties conferred by irreversibly adsorbed material, which can not only adsorb ions itself but, being ampholytic, can dissociate in a manner depending on the *p*H value.

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[1] See the general discussion on colloidal electrolytes in *Trans. Faraday Soc.*, **31**, Part I. (1935), and Hedges, *J. Soc. Chem. Ind.*, **51**, 937 (1932).

[2] Ostwald, *Kolloid-Z.*, **45**, 56, 114, 331 (1928); Verwey, "Hydrophobic Colloids" (Utrecht, 1937), p. 70; *Trans. Faraday Soc.*, **36**, 193 (1940) on oriented dipole-molecules and polarisation effects.

[3] Lederer, Dannmeyer and Schubert, *Kolloid-Z.*, **67**, 63 (1934); Jesen and Gortner, *J. Phys. Chem.*, **36**, 3138 (1932).

[4] *Trans. Faraday Soc.*, **29**, 775 (1933).

[5] Cf. Stoops, *J. Phys. Chem.*, **35**, 1704 (1931).

[6] *Trans. Faraday Soc.*, **29**, 1181 (1933).

[7] *J. Dairy Sci.*, **18**, 21 (1935). See also Moyer, *J. Biol. Chem.*, **133**, 29 (1940).

CHAPTER IV

EMULSIFYING AGENTS

MOST of the early work on emulsions dealt with systems in which various oils were dispersed in water, this type of emulsion being known as the oil-in-water (or O/W) type. Wa. Ostwald, in 1910, first drew real attention to the existence of two types of emulsions, pointing out that emulsions of equal volume concentrations, but of opposite types, *i.e.*, oil-in-water and water-in-oil (W/O), would have quite different properties. Emulsions of both types are now common not only in the laboratory, but in technical practice.

In order to prepare concentrated stable emulsions of either the O/W or W/O type, besides the two liquids, a third substance is necessary, known as the emulsifier or the emulsifying or dispersing agent.[1] On the nature of the emulsifying agent depends the type of emulsion promoted. Water-soluble colloidal substances promote emulsions of the O/W type, whilst oil-soluble colloids promote the reverse type. The theory underlying this is treated in Chapter VI.

The patent literature continues to describe a very large number of emulsifying agents, claimed often for specific purposes in technical operations in such diverse fields as foods, leather, lubricants, polishes, textiles, pharmacy, road emulsions, etc. Some of these patented compounds of great interest for the physical chemist, *e.g.*, the alkyl sulphuric acid esters.

In making an emulsion the primary question may concern the choice of the emulsifying agent, restrictions being imposed on the grounds of edibility, cost, liability to fermentation, or resistance to freezing, boiling, acids or alkalies. A further question obviously concerns the order of efficiency of emulsifying agents.

OIL-IN-WATER EMULSIONS

The usual hydrophilic colloids—proteins,[2] gums,[3] starch,[4] tannic acid,[5] pectin,[6] saponins,[7] bile salts,[8] and plant infusions [9]—have long been recognised as emulsifying agents, often in the preparation of food and pharmaceutical emulsions.

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[1] For summaries see: Ruemele, *Pharm. Zentralhalle*, **75**, 749 (1934); Dubrisay, *Chimie et industrie*, **35**, 267 (1936); Giordano, *Rev. centro estud. farm, bioquim.*, **27**, 183 (1937).

[2] Ghellerova, *Chimie et industrie*, **42**, 868 (1939) deals with casein. Blood serum: Firma Moskovits Mór és Fia, Holland, **2**, 269 (1918).

[3] Gum arabic: Schwarz, *Seifensieder-Ztg.*, **65**, 634 (1938); Musher, U.S. 2,179,518 (1939). Gum tragon: Levin, U.S. 2,170,417 (1939); Schwarzkopf, Ger. 564,046 (1930). Gum tragacanth: Brown and Hoff, U.S. 2,189,854 (1940); Irish moss: Griffith, U.S. 2,171,428 (1939); Wilcken, Brit. 405,906 (1934).

[4] Halward and Murânyi, Fr. 836,354 (1939).

[5] Schulman and Cockbain, *Trans. Faraday Soc.*, **36**, 664 (1940).

[6] Brandrup, *Pharm. Zentr.*, **75**, 421 (1934); Epstein, U.S. 1,737,365 (1929); Patteson, U.S. 1,726,364 (1929); California Fruit Growers' Exchange, Brit. 369,518 (1930); Deiglmayr, Ger. 575,922 and 585,586 (1934); Preiser, Brit. 486,463 (1938); Rosenfeld, Brit. 500,281 (1939).

[7] Brandrup, *Pharm. Zentr.*, **75**, 129 (1934); Verstraete, *J. pharm. belg.*, **21**, 198 (1939).

[8] Hattori, U.S. 1,732,176 (1930). See also Evers and Smith, *Quart. J. Pharm. Pharmacol.* **13**, 213 (1940) and Sobotka, *Pubs. Am. Assoc. Advancement Sci.*, No. **7**, 54 (1939).

[9] Weber and Legoix, *J. pharm. chim.*, **25**, 24 (1937).

The familiar hydrophilic colloids—proteins, gums, carbohydrates—have long been recognised as efficient agents for promoting emulsification of oils and fats in water.

Somewhat detailed investigations have been carried out by Krantz and Gordon[1] on the use of gum acacia and gum tragacanth, with particular reference to the effect of the hydrogen ion concentration of the aqueous phase. Distilled water was brought to a desired *p*H value by the addition of NaOH or HCl and cottonseed oil or Nujol was dispersed therein to the extent of 25 per cent. by volume. To effect such emulsification, there was employed 0·5 grm. of gum tragacanth or 2·5 grm. of gum acacia for 40 c.c. of emulsion.

With gum acacia the emulsions with both vegetable and mineral oil were stable over the *p*H range 2–10. Alkalies were detrimental. The globules were far more uniform and smaller than with gum tragacanth, and on the acid and the alkaline side, a slight increase in size—due to coalescence preceding separation—coincided with minimum stability.

Using gum tragacanth, the emulsions were especially stable in the region *p*H 1·9–2·3, but rapid separation occurred on the alkaline side. It was concluded that the *p*H changes influence the permanency of the gum gel. "Only those tragancanth gels between *p*H 0·4–2·1 remain free from the separation of the water at the surface ; however, the liquids between *p*H 1 and 2·1 prepare the most stable gels with tragacanth," and the stable range for the emulsions coincides with this range.

Krantz correlated the above data with the buffer capacities of the gums. Since gum acacia contains the K, Ca and Mg salts of the weak acid, arabic acid, its buffer is more pronounced in the neutralisation of acids than the neutralisation of alkalies. The experimental results agreed with the fact that the instability of the emulsions commences on the alkaline side at a lesser concentration of alkali than it does on the acid side with a corresponding concentration of acid. The buffering capacity of gum tragacanth seems to play as important a part in the stability of emulsions as it does with gum acacia, but, in this case, the stability of the gum tragacanth gel is the principal factor in stability.

Later, Krantz extended his research to determine the stability of mineral oil emulsions with these gums, employing buffered solutions as the continuous medium. With gum acacia, the stability was unaffected in the *p*H range 2–10·5, but with gum tragacanth the most stable *p*H range with a buffered external phase was 2–5, in contrast to the fact that without a buffered external phase the emulsion stability was optimal at *p*H 2.

GELATIN AS EMULSIFYING AGENT

Gelatin is a useful emulsifying agent for food and medicinal emulsions, provided the nature of the protein is known and understood. It is mentioned frequently in the patent literature,[2] whilst detailed accounts of laboratory experimental work have been given by Briggs and Schmidt,[1] Holmes and Child,[2] Nugent,[3] Narwani,[4] and others.[5]

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[1] *J. Am. Phar. Assoc.*, **15**, 93 (1926) ; **19**, 1181 (1930).

[2] Thus : Dewsbury and Davies, Brit. 431,360 (1935) ; Valentine, U.S. 1,804,135 (1931).

The relation between the *p*H value of the gelatin solution and its emulsification efficiency for pure paraffin oil has been studied by Limburg.[6] Measurements were made of the cataphoretic velocity of the oil globules, and the *p*H values were determined electrometrically. The *p*H values were reached by using the following electrolytes :—

*p*H = 2·8 0·001395 N.HCl.
*p*H = 4·7 acetic acid + sodium acetate (total concentration 0·002 N).
*p*H = 5·5 acetic acid + sodium acetate (total concentration 0·002 N).
*p*H = 9·6 0·00072 N.K_2CO_3.

The results obtained are tabulated below and expressed graphically in Fig. 18.

TABLE 12

CATAPHORESIS OF GELATIN-COATED OIL GLOBULES

Gelatin Concentration in per cent.	Cataphoretic Velocity in μ/sec. Volt/cm.			
	pH = 2·8	pH = 4·7	pH = 5·5	pH = 9·6
0·000	− 3·48	− 4·41	− 4·67	− 8·05
0·00000039	− 1·33	—	—	—
0·00000098	− 0·25	—	—	—
0·00000196	+ 1·25	—	—	—
0·0000098	—	− 2·27	− 3·87	− 6·55
0·000098	+ 3·17	− 0·13	− 3·37	− 5·62
0·00098	+ 3·22	+ 0·07	− 1·59	− 4·32
0·0098	+ 3·13	− 0·07	− 1·50	− 3·32

From the curves it is evident that with sufficient gelatin present a steady minimum value is reached for the cataphoretic velocities. At *p*H = 4·7 (the iso-electric point) a zero value attains. One can assume, therefore, that the oil globules are enveloped with a gelatin layer. At low concentrations of gelatin this layer is incomplete. The graphs show that for complete envelopment of the oil globules, the gelatin concentration required is a function of the *p*H value, increasing with increasing *p*H values. Approximately the relations are :—

*p*H 2·8 requires 0·00064 gr./litre.
*p*H 4·7 ,, 0·00125 ,,
*p*H 5·5 ,, 0·01 ,,
*p*H9·6 ,, 0·1 ,,

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[1] *J. Phys. Chem.*, **19,** 478 (1915).
[2] *J. Am. Chem. Soc.*, **42,** 2049 (1920).
[3] *Trans. Faraday Soc.*, **17,** 703 (1922).
[4] *Kolloid-Z.*, **70,** 297 (1935).
[5] Bresler, Katz and Kremnev, *J. Phys. Chem.* (*U.S.S.R.*), **5,** 602 (1934).
[6] *Rev. trav. chim.*, **45,** 772, 854, 875 (1926).

The negatively-charged gelatin ion will, of course, be adsorbed much less readily than the positively-charged gelatin ion.

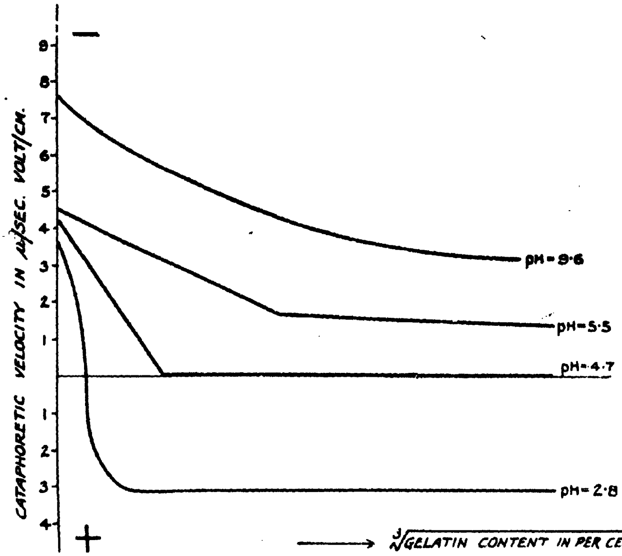

FIG. 18.—Efficiency of gelatin as an emulsifying agent (Limburg).

The stability of the emulsions was investigated by Limburg, all the samples being stirred continuously. The reproduced graphs (Fig. 19) indicate the stability in relation to gelatin content. All the curves show a minimum, the sharpness being a function of pH. The more acid the solution, the steeper is the minimum. The electric charge on the globules is the real factor determining the stability. For solutions with $p\text{H} < 4{\cdot}7$, the charge is fixed. The gelatin concentration at which the charge is zero coincides with that at minimum stability, so that

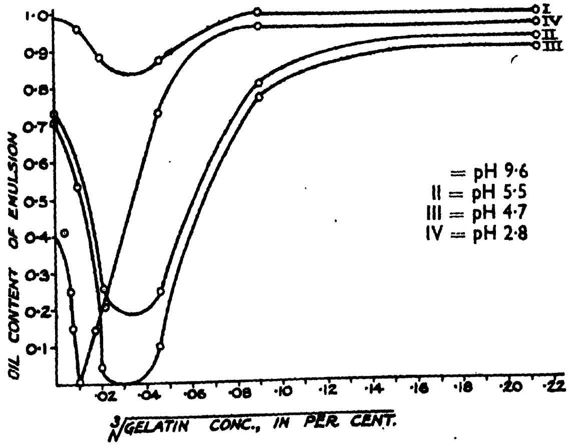

FIG. 19.—Stability of emulsions stabilised by gelatin (Limburg).

instability of the emulsion must be ascribed to the discharge. In solutions with $pH > 4{\cdot}7$, although the first additions of gelatin cause a decrease in the charge, the sign always remains negative. Hence, the minimum stability of the emulsion represents the balance between the diminution of the charge and the protective enveloping of the oil globules, the latter soon conferring marked stability.

Investigations by Friedman and Evans [1] showed that variation of concentration between 0·25 and 1·5 per cent. of gelatin has little effect on the stability of emulsions of various organic liquids in water, at the pH values : 3, 4·7 and 6. The outstanding exception to these findings was the case of 0·25 per cent. of gelatin at $pH = 3$, where the stability of some of the emulsions was greatly decreased. When the pH value of the gelatin solution is changed, the emulsifying capacity is affected in a manner closely related to the changes in the surface tension and the viscosity of gelatin solutions with pH. In this connection it is interesting to note that Zhukov and Bushmakin [2] observed maximum stability of benzene emulsions stabilised with gelatin at the iso-electric point, *i.e.*, where the surface tension and viscosity are at a minimum. Two minimum stability points were observed at pH 2·5 and pH 9·5, coinciding with maximum viscosities. It is concluded that non-hydrated and undissociated gelatin molecules serve best for emulsification.

Different workers have reported varying results as to the efficiency of gelatin in stabilising emulsions, and this must be attributed in part to a non-recognition of the influence of the pH value of the system, and in part to the diversity of grades of gelatin employed. More and more it is being realised that the biological origin and the chemical preparation of gelatins profoundly affect the physical properties.[3]

Kernot and Knaggs [4] prepared low-ash (0·02 per cent.) gelatins from calf skin, bone, horn-pith and fish skin. Emulsions were made with medicinal paraffin, soya bean oil, cod-liver oil and shark-liver oil, the last three freed from free fatty acids. It was noted that highly purified gelatins possess better emulsifying powers than gelatins containing degradation products, whilst fish gelatins were superior to bone gelatins. " The nature of the precursor and the treatment to which it is subjected before the gelatin is extracted have a marked effect on the emulsifying power of the gelatin." The viscosity, which depends on the previous history of the precursor, closely parallels the emulsifying power. Gelatins made from alkali-treated precursors are better emulsifiers and they also possess greater viscosity in solution.

It should be recognised that gelatin is not a strict chemical entity, but is a material which differs in behaviour according to its source and manner of preparation, and which in solution yields different molecular species of varying molecular weights. Briefer's [5] observations on the possible wide range for the iso-electric point of gelatin is of importance here and has been followed up by several papers by Tice[1] who states that gelatin from acid-treated precursors, having an iso-electric point at *p*H 8, requires a *p*H of about 3 effectively to stabilise an emulsion; gelatin from alkali-treated precursors, having an iso-electric point at *p*H 4·7, requires a *p*H of approximately 1.

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[1] *J. Am. Chem. Soc.*, **53**, 2898 (1931).
[2] *J. Russ. Phys. Chem. Soc.*, **59**, 1061 (1927).
[3] Briefer and Cohen, *Ind. Eng. Chem.*, **20**, 408 (1928).
[4] *J. Soc. Chem. Ind.*, **47**, 96 T. (1928).
[5] *Ind. Eng. Chem.*, **21**, 266 (1929).

Replacing the free amino groups in gelatin by hydroxyl and methylene-imino groups considerably alters the emulsifying capacity. The former, as shown by Knaggs,[2] decreases the relative viscosity and at the higher concentrations enhances the emulsifying power, whereas, in general, the latter has just the opposite effect.

COMPLEX ORGANIC EMULSIFYING AGENTS

Based on the idea of molecular orientation at the liquid/liquid interface, an astonishing number of complex organic compounds continues to enter the patents granted in many countries. The general principle is the introduction of polar groups in compounds, whereby the resulting compounds acquire surface-active properties of value as emulsifying agents, wetting agents, dyeing assistants and so forth. It is impossible within the limits of this volume to list all such compounds and only certain very general classes are outlined, serving to illustrate the type of work done and to mention the outstanding commercial branded compounds. Others have published extensive tables of the majority of recognised compounds with some indication of their make-up and uses.[3]

The introduction of polar groups into organic compounds of molecular weight sufficiently great to bring the compounds into the realm of colloidality obviously offers a very wide range of possible emulsifying agents. The gradual change in physical and chemical characteristics according to position in an homologous series is frequently a feature in the specifications covering patented emulsifiers.

SULPHONATION PRODUCTS

In a study of the behaviour of soaps in solution, Reychler[4] described the soap-like character of cetyl sulphonic acid, $C_{16}H_{33}SO_3H$, and its Na salt. He very clearly indicated the effect of introducing the hydrophilic group SO_3H, which possesses properties contrasting with the hydrophobic character of the main organic molecule. Micelle formation in solution was attributed to the water-soluble group. Later[5] he described triethylcetylammonium iodide, $(C_2H_5)_3C_{16}H_{33}NI$, and diethylcetylammonium hydrochloride, $(C_2H_5)_2C_{16}H_{33}HNCl$. The emulsifying powers of these compounds he attributed to the hydrophilic groups present, *i.e.*, to polar groups. The idea of a " balance " between the polar and non-polar groups is definitely to be read into his account (see p. 127).

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[1] *J. Am. Pharm. Assoc.*, **24**, 1062 (1935); *Am. J. Pharm.*, **111**, 4 (1939); *Am. Perfumer*, **42**, (1), 51 (1941). See also Grill and Hogach, *J. Am. Pharm. Assoc.*, **28**, 33 (1939).

[2] *J. Soc. Chem. Ind.*, **51**, 61 T. (1932).

[3] Duncan, *Ind. Eng. Chem.*, **26**, 24 (1934); Van Antwerpen, *ibid.*, **31**, 66 (1939); **33**, 16 (1941). A series of papers in *ibid.*, **31**, 31–57; 64; (1939) is of interest. Duemling, *Arch. Dermatol. Syphilol.*, **43**, 264 (1941), deals with wetting agents (new synthetic chemicals) in dermatologic therapy. See also Lottermoser and Flammer, *Kolloid-Beihefte*, **45**, 359 (1937); Chwala, *Osterr. Chem.-Ztg.*, **40**, 39; 270 (1937).

[4] *Kolloid-Z.*, **12**, 277 (1913). See also Norris, *J. Chem. Soc.*, **121**, 2161 (1922), and Nishizawa, *J. Soc. Chem. Ind. Japan*, **35**, Suppl. binding, 550 (1932).

[5] *Kolloid-Z.*, **13**, 252 (1913).

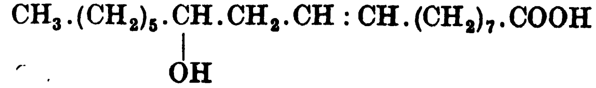
Sulphonation of organic compounds [1] is the basis of a great number of patented compounds classed as " wetting, foaming, penetrating, emulsifying and dispersing agents " (the colloid-chemical principles of such phenomena being intimately related).

The modern physical chemistry of sulphonated fatty acids and alcohols is too extensive for summary here but should be read by the student dealing with them in emulsion investigations.[2]

SULPHONATED OILS

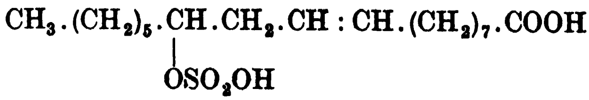
Since Runge, in 1934, discussed the use of sulphonated olive oil in treating cotton, research has continued into the mechanism of sulphonation and the use of the products. Most familiar is Turkey-red oil, prepared by sulphonating castor oil and neutralising the ricinoleic-sulphuric acid with ammonia, alone or mixed with soda or potash. Treatment of the oils with sulphuric acid leads to saponification, sulphonation, oxidation, polymerisation, etc. The products thereby are not stoichiometric compounds, but vary in comparison according to the conditions of their formation.[3]

The complex reactions occurring probably result in Turkey-red oil containing such products as ricinoleic acid, ricinoleic-sulphuric acid, di- to poly-ricinoleic acids and their sulphuric esters and derivatives of dihydroxystearic acid. In sulphonated ricinoleic acid the sulphur is linked to carbon by means of oxygen, giving a sulphuric acid ester. Thus :



$$\mathrm{CH_3.(CH_2)_5.\underset{\underset{\displaystyle OH}{|}}{CH}.CH_2.CH:CH.(CH_2)_7.COOH}$$

with H_2SO_4 gives :



$$\mathrm{CH_3.(CH_2)_5.\underset{\underset{\displaystyle OSO_2OH}{|}}{CH}.CH_2.CH:CH.(CH_2)_7.COOH}$$

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[1] A detailed list of patents is given by van der Werth, " Neure Sulphonierungsverfahren " (Berlin, 1936).

[2] Biffen and Snell, *Ind. Eng. Chem., Anal. Edn.*, **7**, 234 (1935); Hazlet, *J. Am. Chem. Soc.*, **59**, 287 (1937); Tartar and Wright, **61**, 539 (1939); McBain, *Proc. Roy. Soc.*, **A.**, **170**, 415 (1939); Ekwall, *Finska Kemistsamfundets Medd.*, **48**, 8 (1939); Hartley, *Trans. Faraday Soc.*, **34**, 1283 (1938); *Kolloid-Z.*, **88**, 22 (1939); *J. Am. Chem. Soc.*, **58**, 2347 (1936); *Trans. Faraday Soc.*, **32**, 795 (1936); Sisley, *Rev. gen. mat. color.*, **43**, 217 (1939); *ibid.*, **42**, 349 (1938); *ibid.*, **44**, 27 and 66 (1940); Reed and Tartar, *J. Am. Chem. Soc.*, **58**, 322 (1936); Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939); Stirton, Perterson and Groggins, *Ind. Eng. Chem.*, **32**, 1136 (1940); Kimura, Nakano and Tantiguti, *J. Soc. Chem. Ind., Japan*, **42**, Suppl. binding, 121–8 (1939).

[3] See Dean, " Utilization of Fats " (London : 1938), p. 282, and Burton and Robertshaw, " Sulphated Oils and Allied Products " (London : 1939). An early account is given by Matsumoto, *Rept. Imp. Ind. Lab. Osaka*, **4**, (viii), 1–35 (1923). A review of the factors affecting sulphonation is by Kadmer, *Seifensieder-Ztg.*, **62**, 180 and 207 (1935); see also Welwart, *ibid.*, **62**, 707 and 731 (1935). Koppenhoefer deals with the chemical constituents of sulphated oils, *J. Am. Leather Chem. Assoc.*, **34**, 622 (1939). Analytical determinations are described by Hart, *Ind. Eng. Chem. Anal. Edn.*, **7**, 137 (1935); *Proc. Am. Assoc. Textile Chem. Colorists* **1935**, 180; *Ind. Eng. Chem. Anal. Edn.*, **9**, 177 (1937).

The emulsifying powers of sulphonated oils have been investigated by Bumcke,[1] Nishizawa,[2] Ruemele,[3] and Hart.[4] This last worker found that sulphonated oils are better emulsifiers for mineral than for fatty oils; in this respect, acid sulphonated castor oil is inferior to acid sulphonated olive oil. Complete neutralisation of a sulphonated oil decreased its miscibility with neutral oils, but the addition of alcohol restored the emulsifying power towards mineral oils.

Later research [5] resulted in true sulphonic acids, sulphur being linked directly to carbon, and then to compounds designed to "block" the reactive COOH group,[6] which adversely influenced the products, *e.g.*, hard water forming calcium salts. Thus, sulphonation of the butyl ester of ricinoleic acid yields the group $COOC_4H_9$ in place of COOH; again, the acid amide group $CONH_2$ can be prepared, as in the commercial Humektols. Igepon-T is another example of amidation, being the Na salt of the amino derivative of oleic acid and taurine (amino-ethanesulphonic acid), *i.e.*, $C_{17}H_{33}.CO.NH.CH_2.CH_2.SO_3Na$. The related product,[7] Igepon-A, is the sodium salt of the oleic derivative of isethionic acid (β-hydroxyethyl sulphonic acid), *i.e.*,

$$CH_3.(CH_2)_7.CH:CH.(CH_2)_7.COO.CH_2.CH_2.SO_3Na.$$

Reduction of the COOH group to an alcoholic group is utilised in the commercial Texapons.

Since complete elimination of the COOH group was found desirable, alkyl sulphuric acid esters have been prepared by sulphonating higher alcohols:

$$C_nH_{2n+1}OH \longrightarrow C_nH_{2n+1}OSO_2OH.$$

The colloid properties of these products in aqueous solution have been investigated by Lottermoser and his co-workers.[8]

The sulphonated fatty alcohols [9] possess excellent wetting-out properties and emulsifying capacities, and are stable to acids, alkalies and sea water. The fatty alcohols are prepared by catalytic hydrogenation under high pressure of artificially prepared esters of the corresponding fatty acids and of naturally occurring esters (glyceryl esters or fats), and of the free fatty acids themselves.

Five important early patents relating to the above are:—

(1) Non-carboxylated alcohols above C_8, *e.g.*, cetyl alcohol (hexadecyl alcohol = $C_{16}H_{33}OH$) which occurs as the palmitic ester in spermaceti,

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[1] *J. Am. Leather Chem. Assocn.*, **22**, 621 (1927).

[2] *Tech. Repts. Tohoku Imp. Univ.*, **10**, 116 (1931).

[3] *Seifensieder-Ztg.*, **62**, 393 (1935).

[4] *Ind. Eng. Chem.*, **21**, 85 (1929); *Ind. Eng. Chem. Anal. Edn.*, **4**, 119 (1932).

[5] Summaries of such work are given by: Stewart and Bunbury, *Trans. Faraday Soc.*, **31**, 208 (1935); Briscoe, *Ind. Chemist*, **8**, 67 (1932) and *J. Soc. Dyers Colourists*, **49**, 71 (1933); Killeffer, *Ind. Eng. Chem.*, **25**, 138 (1933); Schrauth, *Seifensieder-Ztg.*, **58**, 61 (1931); Bruinier, *Textile Colorist*, **55**, 456 (1933).

[6] Stadlinger, *Chem. Umschau*, **39**, 217 (1932) and *The Rayon Record*, **6**, 505 (1932).

[7] The Igepons are discussed by: Sweet, *Am. Dyestuff Reptr.*, **23**, 198 (1934); Lederer, *Angew. Chem.*, **47**, 119 (1934); Boedeker, *Melliand Textilber*, **13**, 436 (1932); Nüsslein, *J. Soc. Dyers Colourists*, **47**, 309 (1931) and *Dyer, Calico Printer*, **65**, 320 (1931); *Melliand Textilber.*, **18**, 248 (1937); Kehren, *Z. ges. Textil-Ind.*, **34**, 517 (1931).

[8] *Kolloid-Z.*, **63**, 49, 175 (1933).

[9] See Ohl, *Allgem. Oel-u. Fett-Ztg.*, **32**, 14 (1935) for a review. Also Evans, 3. *Soc. Dyers Colourists*, **51**, 233 (1935).

are sulphonated with sulphuric acid in presence of acetic or other anhydride, with or without a diluent and/or a catalyst.[1]

(2) Alcohols corresponding with the higher fatty acids, *e.g.*, oleyl alcohol, C_8H_{15} . CH : CH . $(CH_2)_7$. CH_2 . OH, are treated with concentrated or fuming sulphuric acid at 0° C., whereby the alcohol group is sulphated and H–SO_4H is added at the double linkage.[2]

(3) Alcohols derived from fatty acids, *e.g.*, oleic, by replacement of COOH by CH_2OH, are sulphonated cold in the presence of acetic anhydride or acetyl chloride.[3]

(4) Waxes, etc., hydrogenated to a practically zero iodine number, are hydrolysed with alkali and the high molecular alcohols are extracted with solvent or are steam-distilled *in vacuo*. Thus, sperm oil yields cetyl and octadecyl alcohols.[4]

(5) A mixture of high molecular alcohols obtained by the catalytic hydrogenation of oxides or carbon under pressure in the synthesis of MeOH is sulphonated. Thus the alcoholic mixture from a MeOH synthesis containing alcohols boiling between 170°–200° C. is treated with H_2SO_4 and oleum.[5]

The mixture of saturated fatty alcohols derived from the hydrogenation of coconut oil, or the free fatty acids thereof, yields the commercial Lorol-Technical [6] (lauryl alcohol = dodecyl alcohol, $C_{12}H_{25}OH$, predominating). Similarly, Lanette wax is derived from the hydrogenation of commercial stearine and contains hexadecyl or cetyl alcohol (C_{16}) and octadecyl or stearyl alcohol (C_{18}). These two products are sulphonated for technical use. A further product is sulphonated Ocenol from the unsaturated fatty alcohol, obeyl (C_{18}). These products are all marketed as the sodium salts of the sulphuric acid esters.

Alkylated naphthalene sulphonic acids, represented by the commercial Neomerpins and Nekals, have been proposed as substitutes for Turkey-red oils. Thus, propylated aromatic sulphonic acids, especially those of naphthalene and other polynuclear hydrocarbons, are obtained by the action of isopropyl alcohol on aromatic sulphonic acids in presence of sulphuric acid.[7]

PETROLEUM SULPHONIC ACIDS

Obtained as by-products in petroleum refining, the sulphonic acids have been used as emulsifying agents.[8] Neyman and Pilat [9] point out that of these acids one group of relatively low molecular weight gives water-soluble Ca salts and another of higher molecular weight gives

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[1] Deutsche Hydrierwerke A.-G., Brit. 307,709 (1929).

[2] H. Th. Böhme A.-G., Brit. 308,824 (1929).

[3] H. Th. Böhme A.-G., Brit. 317,039 (1929).

[4] Deutsche Hydrierwerke A.-G., Brit. 355,484 (1930).

[5] Deutsche Hydrierwerke A.-G., Ger. 535,853 (1929).

[6] Cf. H. Th. Böhme A.-G., Ger. 593,709 (1934) and Brit. 365,938 (1930). Sulphonated Lorol T.A. is the corresponding triethanolamine soap.

[7] Badische Anilin-und Soda-Fabrik., Ger. 336,558 (1917), cf. Felix, U.S. 1,833,245 (1931).

[8] Voogt, U.S. 1,901,383 (1933); Bird and Rosen, U.S. 1,963,257 (1934); Buc and Tate, Canadian 301,507 (1930); Sudfeldt & Co., Ger. 595,987 and 595,604 (1934); Schaefer, *Allgem. Oel Fett-Ztg.*, **29**, 505 (1932); Naphtali, *Fettchem. Umschau.*, **40**, 219 (1933); Petroff, U.S. 1,230,599 (1917).

[9] *Ind. Eng. Chem.*, **26**, 395 (1934); *Petroleum Z.*, **29**, (iii.), 1 (1933).

Ca salts insoluble in water. The Na salts greatly depress the surface tension of water and effect marked reduction in the interfacial tension of toluene/water.

SULPHONATED ABIETENES

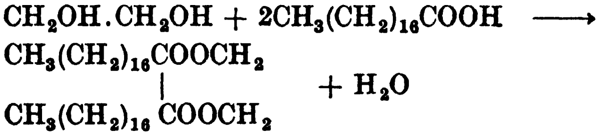
The sulphonated abietenes have been described by Gubelmann, Weiland and Henke,[1] Abietene is produced from wood rosin and is sulphonated with twice its weight of 100 per cent. H_2SO_4 at 10° C. for 20 hours. The sulphonic acid is separated from water as a black oil,, but its alkali metal salts are solids, readily powderēd. Commercially, the Na salt is sold as a brown powder which can be used in neutral, acid or alkaline solution.

Noll [2] has described the various Nekals, where the emulsifying capacity is traced to the presence of different side chains in the benzene, naphthalene or anthracene rings. Nekal A is the crude Na salt of octohydroanthracene-mesa-sulphonic-acid. Nekal BX is the Na salt of a naphthalene sulphonic acid with side chains, whilst Neomerpin is a combination of Nekal A with methylhexalin and is insensitive to Ca, Mg and Fe salts.

Dreyfus [3] has patented esters, amides or esteramides obtained by condensing amino-alcohols with naphthenic or resin acids, *e.g.*, of colophony and various copals or certain synthetic resins. Other agents patented are butylnaphthalenesulphonic acid,[4] isopropylnaphthalenesulphonic acid [5] and their salts.

AGENTS FROM HYDROXY COMPOUNDS

New cheap soaps have become commercially available, produced by the esterification of the glycols with fatty acids : [6]



$$CH_2OH.CH_2OH + 2CH_3(CH_2)_{16}COOH \longrightarrow \begin{array}{l} CH_3(CH_2)_{16}COOCH_2 \\ \qquad\qquad\qquad\quad | \\ CH_3(CH_2)_{16}COOCH_2 \end{array} + H_2O$$

"Diglycol oleate" and "diglycol stearate" are now available.[7] The optimum detergent and emulsifying properties are realised by mixtures of the mono- and di-esters ; accordingly, "diglycol stearate" is a mixture of the mono- and di-stearates.[8]

Diglycol oleate is a lemon-coloured oily liquid, insoluble in water, but soluble in alcohol, esters, oils and hydrocarbons. It has a *p*H value of 6·2. It is used for making soluble oils employed in cleaners, lubricants, polishers, sprays and leather fat-liquors. A typical W/O emulsion is furnished by 10 parts of diglycol oleate, 50 parts of turpentine and 100 parts of water. Addition of 0·5 part of NaOH effects a similar but O/W emulsion.

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[1] *Ind. Eng. Chem.*, **23**, 1462 (1931).

[2] *Seifensieder-Ztg.*, **54**, 769, 787, 824, 843, 860 (1927).

[3] Brit. 390,166 (1933) and 394,657 (1933).

[4] Dobmaier, U.S. 1,822,957 (1931) ; Günther, U.S. 1,836,588 (1931).

[5] Pospiech, U.S. 1,817,205 (1931) ; Günther, U.S. 1,843,420 (1932).

[6] Bennett, Canadian 322,765 (1932) and U.S. 1,914,100 (1933) ; *Ind. Chemist*, **8**, 223 (1932). See also Oda, *J. Soc. Chem. Ind. Japan*, **35**, 515 B (1932).

[7] Glyco Products Co. Inc., New York. The London agents are Messrs. Rex Campbell & Co., Ltd.

[8] Cf. Schrader, U.S. 1,826,900 (1931).

Diglycol stearate is a white, wax-like solid, melting at about 55° C. It disperses completely, on stirring, in hot water. It is soluble in hot solvents, oils and alcohols. A 3 per cent. dispersion in water has a *p*H value of 5·4. For cosmetic emulsions or polishes, this agent is melted with the oil or wax and hot water is dispersed therein.

Commercial examples of esters of polyhydric alcohols with fatty acids of high molecular weight, where the alcoholic radicals of the esters still contain non-esterified OH groups, are Emulgator 157 and Tegin, prepared by Th. Goldschmidt A.-G., of Essen.[1] Emulgator 157 is a wax-like substance of an ivory colour, melting at 35°–40° C., promoting emulsions of the O/W type, for use in cosmetics. For the preparation of liquid emulsions a proportion of one part of olein to three parts of Emulgator is required, whilst for creams stearine replaces the olein. Tegin is a wax-like substance melting at 57° C. If it be agitated with ten times its weight of water at 70°C., it immediately forms a very stable O/W emulsion, which on cooling forms a firm cream, suitable for cosmetic preparations. Mixtures of the above esters with acylated alkylene diamines form the basis of Tegacid, which also promotes O/W emulsions which are stable towards acids.

AGENTS FROM HYDROXY ALKYL BASES

Considerable interest has recently been given to amines derived from dihydric alcohols, the hydroxyethylamines or ethanolamines.[2] The three ethanolamines are viscous, colourless liquids, miscible with water and alcohol, but only slightly soluble in ether or benzene. They are :—

Mono-ethanolamine ($H_2NCH_2CH_2OH$). B.P. 171° C. at 757 mm.
Di-ethanolamine ($HN(CH_2CH_2OH)_2$). B.P. 217° C. at 150 mm.
Tri-ethanolamine ($N(CH_2CH_2OH)_3$) B.P. 277° C. at 150 mm.

Tri-ethanolamine has a density of 1·13 and a viscosity of 2·5 poises at 25° C. Commercially, it is the most common and is marketed as a mixture of 75 to 80 per cent. of the tri-, 20 to 25 per cent. di-, and 0 to 5 per cent. mono-ethanolamine. Combination with fatty acids in molecular proportions yields soaps which are excellent emulsifying agents of oils intended for cutting oils, oil sprays, etc. When 28 parts of oleic acid and 15 parts of tri-ethanolamine are mixed cold the result is transparent soap, very soluble in water. With solid soaps like stearic, heating is required to effect saponification. Emulsions prepared with tri-ethanolamine soaps are fine-grained and stable and are neutral in reaction. Usually from 2 to 4 parts of tri-ethanolamine per 100 parts of oil are needed with fatty acid 2 to 5 times the amount of tri-ethanolamine.[3]

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[1] London agents : A. Boake Roberts & Co. Ltd. The brand name is ABRACOL, *e.g.*, Tegin is now Abracol G.M.S.

[2] I. G. Farbenind. A.-G., Fr. 646,816 (1928) ; Steinfels Soc. Anon., Fr. 717,390 (1931) ; Bennett, Brit. 420,760 (1933). See Smith, *Soap*, **7** (xii.), 27 (1931) ; Navarre, *Am. Perfumer*, **27**, 650 (1933).

[3] See Wilson, *Ind. Eng. Chem.*, **22**, 143, (1930).

A number of workers have described the alkylamines,[1] including tri-ethanolamine naphthenate.[2] General Metallurgical and Chemical Limited announce iso-propanolamine in substitution of tri-ethanolamine.[3] The cyclic ether amine, morpholine,[4] forms soaps with fatty acids which are excellent emulsifying agents.[5]

Hartmann and Kägi[6] hold a patent for acylated diamines such as hydrochlorides or acetates of diethylaminoethyliminodicarboxylic acid, linoleylethylethylenediamine, or similar compounds.

Regarding this patent, Hartmann and Kägi[7] point out that the higher fatty acid N-carboxyl derivatives of asymmetrically substituted ethylenediamine yield readily soluble neutral salts with most inorganic and organic acids possessing the properties of soaps. The salts are viscous liquids in the anhydrous condition, and their aqueous or acid solutions form a foam even at great dilution, the limit being at 0·5 part per million. Addition of alkali effects precipitation of the base and destroys the foaming capacity, while the salt is precipitated in a colloidal hydrated form from concentrated solution on addition of NaCl. The aqueous solutions of the salts have remarkable emulsifying powers and they depress the interfacial tension, oil/water, to a remarkably low value. In certain cases where sensitivity to alkali is objectionable, the base is converted into a quaternary NH_4 base, stable to alkali, by heating with methyl chloride, dimethyl sulphate or a similar substance.

Other instances of the introduction of polar groups into organic compounds are provided by saponification of oxidation products of paraffin hydrocarbons,[8] the chlorination of oxidised animal, vegetable or mineral waxes,[9] and compounds of xanthic acid $CS(OC_2H_5)SH$, *e.g.*, potassium laurylxanthate.[10]

Under the name of Tylose S, the I. G. Farbenind. A.-G. has marketed[11] a material on a water-soluble methyl cellulose base, which is a neutral emulsifying agent, resistant to alkali. The solutions which it gives have an external appearance similar to that of a mucilage of gum tragacanth. Tylose S is dissolved by the addition of boiling water and subsequent stirring until cold. Solutions of 1–2 per cent. concentration possess very marked emulsifying powers. An important feature of this agent is its immunity to fermentation.

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[1] Fischer, *Allgem. Oel-u. Fett-Ztg.*, **32**, 489 (1935); Ruemele, *Seifensieder-Ztg.*, **62**, 657 (1935); Fischer, "Triäthanolamin und andere Aethanolamine" (Berlin: 1937); Cupples, *J. Econ. Entomol.*, **31**, 68 (1938); Ohl, *Monatsh. Seide Kunsteide Zellwolle*, **43**, 498 (1938); Fiero, *J. Am. Pharm. Assoc.*, **28**, 284 (1939).

[2] Pleteneva, *Trans. Sci. Inst. Fertilizers Insectofungicides* (*U.S.S.R.*), **135**, 73 (1939).

[3] *Manfg. Chemist*, **1940**, 84.

[4] Carbide and Carbon Chemicals Corporation.

[5] Wilson, *Ind. Eng. Chem.*, **27**, 867 (1935).

[6] U.S. 1,527,869 (1925).

[7] *Z. angew. Chem.*, **41**, 127 (1928). See also Kaiser and Eggensperger, *Pharm. Ztg.*, **77**, 896 (1932).

[8] Eisele and Graf, Ger. 548,442 (1927); I. G. Farbenind. A.-G., Ger. 564,922 (1931) and 566,797 (1930).

[9] I. G. Farbenind. A.-G., Ger. 545,094 (1928) and Brit. 321,239 (1928).

[10] Deutsche Hydrierwerke A.-G., Brit. 369,977—8 (1930).

[11] London agents: Messrs. J. M. Steel and Co., Ltd. See also Deutsche Hydrierwerke A.-G., Ger. 573,291 (1930). See Clemens and Read, *Australian J. Pharm.*, **20**, 191 (1939); Dultz, *Deut. Apoth.-Ztg.*, **55**, 524 (1940).

Ammonium linoleate is marketed by Glyco Products Co. Inc. as Emulsifier B-585, whilst Commercial Solvents Corporation feature butyl acetyl ricinoleate.[1]

MISCELLANEOUS BRANDED COMPOUNDS

From the very numerous organic compounds now commercially available several of the more prominent will be mentioned :—

Aerosols (American Cyanamid and Chemical Corporation) are esters of sodium sulphosuccinic acid such as Aerosol AY (diamyl ester), Aerosol IB (dibutyl ester), Aerosol MA (dihexyl ester), and Aerosol OT (dioctyl ester). These agents were patented by Jaeger [2] and have been very well described by Caryl and Ericks,[3] who employed the Draves test for wetting measurements. McBain and Sharp [4] have shown that when the surfaces of solutions of Aerosol OT are suitably reduced in area, a pellicle is formed which will not dissolve unless a definite pressure is exceeded. For dilute solutions (0·01–0·001 g./litre) this pressure is at a maximum for a surface 75 per cent. compressed. If the pellicle is a polymolecular film, it must buckle and expose soluble groups.

Alphasol AY, sulphonated ester of a dicarboxylic acid.[5]

Aminohydroxy aliphatics.[6] These nitroparaffin derivatives yield higher fatty acid soaps which are excellent emulsifying agents. Their properties are listed thus :—

	Molecular Weight.	Melting Point, °C.	Boiling Point °C.	Specific Gravity 20·° C./20°C.	*p*H of 0·1 M. Aqueous Solution at 20° C.	Solubility in water—grams per 100 c.c. at 20° C.
2-Amino-1-butanol .	89.14	—2	178 (at 760 mm. of Hg)	0·944	11·11	Completely miscible
2-Amino-2-methyl-1-propanol.	89.14	25 to 26	165 (at 760 mm. of Hg.	0.934	11.27	Completely miscible
2-Amino-2-methyl-1, 3-propanediol.	105.14	109 to 111	151 to 152 (at 10 mm. of Hg)	—	10.78	250
2-Amino-2-ethyl-1, 3-propanediol.	119.16	37.5 to 38.5	152 to 153 (at 10 mm. of Hg)	1.099	10.82	Completely miscible
Tris (hydroxymethyl) aminomethane.	121.14	171 to 172	219 to 220 (at 10 mm. of Hg)	—	10.36	80

Atlas [7] emulsifying agents are partial fatty acid esters of polyhydroxy substances, the hexahydric alcohols, mannitol and sorbitol. Most of these are mono- or di- fatty acids esters, the majority having a hydroxyl number of not less than 100. In general the mono-esters are the most efficient emulsifying agents, tending to form O/W emulsions with vegetable and animal oils, but W/O emulsions with mineral oils. The agents are listed by number prefixed by G, such as

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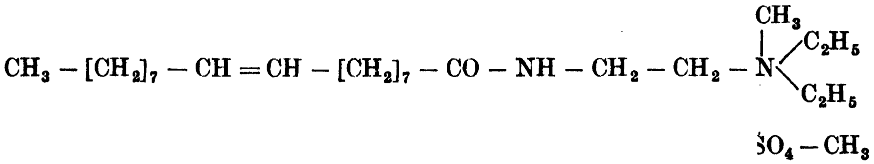
[1] See Knight, U.S. 1,937,969 (1933) and Oranienburgher Chem. Fab. A.-G., Ger. 540,065 (1928).
[2] U.S., 2,028,091 (1936).
[3] *Ind. Eng. Chem.*, **31**, 44 (1939).
[4] *J. Am. Chem. Soc.*, **63**, 1425 (1941).
[5] See Cupples, *Soap*, **15** (ix), 41 (1939).
[6] Commercial Solvents Corp.
[7] London : Honeywill and Stein, Ltd.

No.	Description.	No.	Description.
G–904	Mannitan Monolaurate	G–759	Sorbitan Monolaurate
G–905	Mannitan Monomyristate	G–741	Sorbitan Monomyristate
G–906	Mannitan Monopalmitate	G–742	Sorbitan Monopalmitate
G–908	Mannitan Monostearate	G–909	Sorbitan Monostearate
G–954	Mannitan Monoöleate	G–944	Sorbitan Monoöleate
G–948	Mannide Monoöleate	G–650	Sorbitan Triricinoleate
G–660	Mannitan Monoricinoleate	G–651	Sulfonated Sorbitan Triricinoleate

Daxad,[1] polymerised organic salts of alkyl aryl sulphonic acids.

Gardinol,[2] fatty alcohol sulphate.

Sapamine,[3] such as *Sapamine A*, the diethyl aminoethyl oleyl amide acetate. The corresponding *Sapamine CH* is the hydrochloride and *L* is the lactate. *Sapamine MS* is the methyl sulphate of the corresponding quaternary base, with the formula



$$\mathrm{CH_3-[CH_2]_7-CH=CH-[CH_2]_7-CO-NH-CH_2-CH_2-}\overset{\mathrm{CH_3}}{\underset{\mathrm{SO_4-CH_3}}{\mathrm{N}}}\!\!<{\mathrm{C_2H_5} \atop \mathrm{C_2H_5}}$$

Shirlacrol[4] consists of a fraction of vertical-retort tars distilling between 210° and 270° C. and containing on the average 55–60 per cent. by volume of material distilling below 230° C. These less volatile phenols are used in NaOH solution.

Tergitols are sodium alcohol sulphates prepared by Carbide and Carbon Chemicals Corporation. The numbers are 4 and 7 (sodium salt of higher secondary alkyl sulphate), 08 (sodium salt of higher primary alkyl sulphate) and 4T (amine salt of higher secondary alkyl sulphate). Their wetting efficiency has been studied by Wilkes and Wickert who report extensive surface tension data.[5]

Tritons[6] are synthetic chemicals by Röhm and Haas Co. Inc., and the W–30 compound is particularly useful as a surface-active agent,[6] being a sulphated aromatic ether alcohol. The surface tension at 25° C. of a 0·05 per cent. aqueous solution is 32·8 dynes/cm. and of a 5 per cent. solution 27·5 dynes/cm.

WATER-IN-OIL EMULSIONS

Newman[7] found that unstable emulsions of water in benzene could be prepared by previously dissolving in the benzene such substances as crude rubber (0·2 per cent.), paraffin wax (2 per cent.), rosin (5 per cent.), or sulphur (concentrated solution). Unstable emulsions of water in CS_2 were promoted by spermacetin, gun-cotton, and Ba oleate as emulsifiers. Newman also found that the oleates of Mg, Zn, N, or Ca promoted emulsions of benzene in water. Holmes and Cameron [1] recommend gum dammar. Bennett describes trihydroxy-ethyleneamine distearate.[2]

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[1] See King and Wrzeszinski, *Trans. Faraday Soc.*, **35**, 741 (1939).

[2] Lindner, *Monatschr. Textil-Ind.*, **50**, 65 (1935); Pedersen, *Am. Dyestuff Reptr.*, **24**, 137 (1935).

[3] Hartmann and Kägi, *Z. angew. Chem.*, **41**, 127 (1928). Pfister, *Anales quim. farm.*, **1938**, 14.

[4] Morgan, Pratt and Pettet, *J. Soc. Dyers Colourists*, **49**, 125 (1933); *Dyer*, **69**, 549 (1933).

[5] *Ind. Chem. Eng.*, **29**, 1234 (1937); *India Rubber World*, **99**, (ii), 33 (1938). See also Bredeau, *Rev. Prod. chim.*, **41**, 289 (1938); Perlo, *Papeterie*, **61**, 794 (1939).

[6] U.S. 1,987,228 (1935); 2,008,017 (1935); 2,008,032 (1935); 2,045,517 (1936); 2,072,153 (1937); 2,075,018 (1937).

[7] *J. Phys. Chem.*, **18**, 45 (1914).

Briggs and Schmidt [3] found that over 90 per cent. by volume of water can be emulsified in benzene, using rosin. They also investigated the emulsification of water in benzene by the aid of Mg oleate. By the gradual addition of water to benzene containing 1 per cent. Mg oleate, an emulsion so concentrated as to contain 90 per cent. water was obtained, of a stiff, jelly-like consistency. This emulsion, however, would not remain stable for more than a few hours. Stiff, viscous emulsions of water in benzene were also prepared using Al palmitate, but the water appeared as large irregular drops entangled in a voluminous precipitate of gelatinous character. Such " quasi-emulsions " separated in about 33 minutes. Montan wax readily emulsifies water in petroleum.[4]

In a study of the effect of changes of hydrogen ion concentration upon emulsions of the W/O type, Krantz and Gordon [5] used magnesium oleate as the emulsifying agent to disperse water in olive oil and mineral oil. The systems contained 25 per cent. by volume of water, and 1 grm. of the soap was required with each 40 c.c. batch. The age of the soap is of real importance, ageing leading to hardening and brittleness with consequent poor mixing with the oil and granular unstable emulsions.

The internal phase was distilled water, adjusted in *p*H value with NaOH and HCl or H_2SO_4. Emulsification was effected at 25° C. by trituration. Using freshly-precipitated Mg oleate, the emulsions were stable over the *p*H range 1·87–12·38, although on the alkaline side beyond *p*H 10·97, the degree of creaming was less than when the internal phase was nearer to *p*H 7. With olive oil as the external phase, the emulsions as a whole were more permanent than with mineral oil.

The presence of NaCl in the aqueous phase had no influence with mineral oil, but with olive oil the emulsions had a degree of stability varying inversely as the concentration of NaCl.

Pink [6] has carried out considerable research on W/O emulsions stabilised by magnesium oleate. When water was added to benzene solutions of magnesium oleate, the initial small quantities of water were dissolved, but further additions resulted in practically complete precipitation of the soap in a form containing water. The amounts of water taken up prior to precipitation of the hydrated soap were proportional to the concentration of the magnesium soap. Water was also found to be soluble in benzene solutions of ethanolamine oleate,[1] but after precipitation of the soap in a white curdy form, further water leads to inversion, an O/W system resulting. Pink's conclusion [2] is that the precipitated soap functions as a solid emulsifying agent in W/O emulsions (see p. 138).

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[1] *Colloid Symposium Monograph*, **2**, 137 (1925); U.S. 1,410,012 and 1,429,430 (1922).

[2] *Soap*, **5**, (xi.), 39 (1930).

[3] *J. Phys. Chem.*, **19**, 491 (1915).

[4] Roederer, Ger. 409,690 (1921).

[5] *J. Am. Pharm. Assocn.*, **18**, 797 (1929).

[6] *Thesis* (Belfast, 1940); *J. Chem. Soc.*, 1938, 1252; **1939**, 619; **1940**, 211; *Trans. Faraday Soc.*, **37**, 180 (1941).

Most of the really precision studies on W/O emulsions have coincided with research on the inversion of emulsions and, indeed, certain W/O emulsions cannot be directly prepared owing to the insolubility of the polyvalent metal soaps in water or mineral oil. An inversion process is necessary.

Schulman and Cockbain [3] have published the outstanding paper in this field and they conclude that to obtain directly a W/O emulsion the emulsifying agent must be brought to the dineric interface so as to form a film which is uncharged and rigid. A good example quoted by these authors is the emulsion of nujol-in-water produced by the aid of digitonin (dissolved in water) and cholesterol (dissolved in nujol). A strong complex formation provides a rigid and uncharged interfacial film. (See p. 214).

Lanolin is a well-known agent for preparing W/O emulsions for use in cosmetics and pharmacy.[4] Different fractions of this material possess different emulsifying powers.[5] Protegin [6] is marketed by Th. Goldschmidt A.–G., and contains the emulsifying substance from woolfat by extraction with petroleum jelly.

For ointments, paints and foods, where a W/O emulsion is desired, the addition of 0·1–10 per cent. of phytosterols has been recommended.[7] The most important instance of this type of emulsion occurs in the margarine industry, especially on the Continent. Obviously severe limitations are imposed on the nature of an emulsifying agent for foods. An oxidised vegetable oil serves excellently as emulsifying agent for the dispersion of water in oils. Such an oil is marketed as "Palsgaard Emulsion Oil" or "P.E.O.", sometimes referred to as "Schou Oil."

Schou's emulsifier [8] is prepared by oxidising a refined vegetable oil, *e.g.*, soya bean oil, at 250° C. until gelatinisation occurs. After cooling to 100° C. the gelatinised oil is mixed with twice its volume of cold soya bean oil, yielding a pale brown oil of syrupy consistency. As little as 0·5 per cent. of the emulsifier is required to be dissolved in the melted fatty phase in margarine manufacture to permit the stable dispersion therein of milk and water.

Similarly, Vahlteich [9] recommends slightly blown soya bean oil to prepare W/O margarine emulsions. The raw oil of S.G. 0·925 is air-blown at 80°–120° C. to S.G. 0·935–·955. Steam is blown in at 270°–320° C., the oil being under vacuum. The viscous oil is then used in margarine at the rate of 8 lbs. to 1,000 lbs. of the fatty phase.

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[1] *J. Chem. Soc.*, **1939,** 53.

[2] See Martin, *Trans. Faraday Soc.*, **37,** 199 (1941).

[3] *Trans. Faraday Soc.*, **36,** 665 (1940).

[4] See Barnes, U.S. 1,830,502 (1931).

[5] Powers, Leask and Warner, *J. Am. Pharm. Assoc.*, **29,** 14 (1940).

[6] London agents: M. R. Chemical Products, Ltd.

[7] Sandqvist and Lindström, Brit. 329,305 (1929).

[8] Brit. 178,885; 187,298; 187,299 (1922); Danish 30,741 (1922). See Herlow, Brit. 530,240 (1939).

[9] U.S. 1,975,672 (1934).

Important experiments have been conducted by Mohr and Eichstädt.[1] Oil and skim milk (4/1) were mixed at 40° C. with and without P.E.O., and the type of emulsion determined by observing its electrical conductivity. The resistance of a W/O emulsion was 20,000 ohms, the oil being a non-conductor and the continuous phase. Table 13 gives the results when the oil and the milk were simultaneously poured into the mixing vessel, normally a condition favouring the emulsion type, oil-in-milk.

TABLE 13

CONDUCTIVITY TESTS WITH SCHOU'S OIL

Oil.	Electric Resistance in Ohms.	
	No Emulsifying Agent.	0·5 per cent. Emulsifying Agent.
Oleomargarine . . .	20,000	20,000
Neutral lard . . .	1,375	20,000
Premier jus . . .	8,000	20,000
Hardened whale oil . .	20,000	20,000
Coconut oil . . .	1,190	20,000
Hardened arachis oil . .	2,340	20,000

Accepting, then, the efficiency of oxidised oil to promote W/O emulsions, there is much of interest in the enquiry as to the mechanism of its action.

Smith[2] has observed that cod liver oil on ageing undergoes an oxidation change antagonistic to emulsification as O/W systems. He found that the Donnan drop-number of water falling through the oil increases as the oxidation of the oil advances—*i.e.*, as the tendency towards W/O emulsions grows. Butler[3] has attempted to follow the oxidation changes by measuring the electrical conductivity of cod liver oil itself, but his results do not throw any light on this problem.

The fact that oxidised oils function as emulsifying agents must be attributed to the presence of polar groups in the new large molecules. Cohan and Hackerman[4] report that orange oil (actually orange terpene) readily emulsifies in water when oxidised. The physical chemistry of the oxidation changes is very complex,[5] but the work of Long[6] (Langmuir balance studies on monomolecular films of blown and heat-bodied oils on water surfaces) proves that the introduction of polar groups leads to increased attraction of the gelatinised oils for water.

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[1] *Margarine Industrie* (1927), Nr. 7/8; (1932), Nr. 12/13, 16/17, 18/19, 20/21.

[2] *Quart. J. Pharm. Pharmacology*, **3**, 373 (1930).

[3] *Proc. Iowa Acad. Sci.*, **36**, 299 (1929); **37**, 316 (1930).

[4] *Ind. Eng. Chem., Anal. Edn.*, **12**, 210 (1940).

[5] Dean, " Utilization of Fats (London, 1938), p. 218.

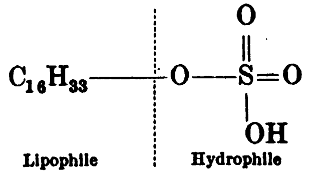
[6] *Ind. Eng. Chem.*, **17**, 138, 905 (1925); **18**, 1245, 1252 (1926); **19**, 62, 901. 903 (1927); **20**, 809 (1928); **21**, 950, 1244 (1929); **22**, 768 (1930); **23**, 53, 786 (1931); **25**, 1086 (1933); **26**, 864 (1934).

BALANCED EMULSIFYING AGENTS

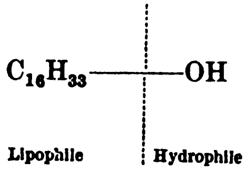
A recent patent[1] fixes attention on the conception of " balance " regarding the polar and non-polar groups in the molecules of emulsifying agents. Primarily the patent concerns anti-spattering agents for incorporation in margarine to enable this fatty food to undergo frying like butter.

The patent specification contains very extensive data relating to numerous organic compounds. An outstanding characteristic of anti-spattering agents is stated to be the presence of balanced lipophile and hydrophile groups. The agents concentrate at the oil/water interface, being oriented therein. Excess of either lipophile or hydrophile character greatly reduces the efficiency of the agent.

To illustrate the matter, palmityl hydrogen sulphate is contrasted with palmityl alcohol, the former being effective and the latter useless as an anti-spattering agent. In the case of the alcohol, the hydrophilic OH group is entirely swamped by the strong lipophilic palmityl radical. The HSO_4 group, on the contrary, confers more pronounced hydrophilic character. Thus :



$C_{16}H_{33}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}=O$



$C_{16}H_{33}-OH$

" It appears that in a given homologous series there is a point or range at or within which lipophile and hydrophile characteristics are so balanced that an optimum power for the prevention of spattering is imparted in the molecule." On either side of this point, one or other of the opposite characteristics predominates. Examples of very effective agents are cholesteryl ester of betaine hydrochloride (carbocholesteroxy) methyl pyridinium bromide, and the Na salt of stearyl diethylene-glycol sulphoacetate. Compounds entirely free from anti-spattering properties are instanced as triethanolamine oleate, isopropyl naphthalene sodium sulphonate and hydroxystearic acid.

The general formula for the desired agents is :

$$[R(O)_w X_v]_z Y$$

where R = lipophile residue, O = oxygen, w, v and z are whole numbers, Y = an innocuous cation, and X = sulphur in the form of its oxygen acid radicals.

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[1] Epstein and Harris, U.S. reissue 21,683 (1941), being reissue of U.S. 1,917,253 (1933) claiming a salt of monostearin sulphoacetate and a monostearic ester of glycerol. See Harris, U.S. 1,917,256 (1933), reissue 19,425 (1935); Brit. 366,909; 378,372; 378,373 (1932). Harris, 2,212,521 (1940). Kritchevsky, U.S. 2,195,713 (1940). See also: Schou Brit. 474,717 (1937); 494,639 and 496,166 (1938); Lever Bros., Brit. 439, 435 (1935); 442,950 (1936); Lundsgaard, Brit. 455,540 (1936); Emulsol Corporation, Brit. 452,138 (1936). Undoubtedly a similar idea underlies the use of polar groups in compounds intended to enhance the fluidity of chocolate, as in Brit. 407,248 (1933). Reference should also be made to experiments with compounds of sugar and fatty acids; for example, stearyl-glucose promotes W/O emulsions. Schmaltz, *Kolloid-Z.*, **71**, 234 (1935).

THE EFFICIENCY OF EMULSIFYING AGENTS

It is natural that early investigators should have attempted to arrange the various emulsifying agents in some order of efficiency to promote O/W emulsions.[1] Although mention will be made of some of these attempts, it is to be emphasised that modern opinion disclaims any efficiency grading except under very clearly defined conditions and, even then, with the realisation that many factors operate to render the results only strictly comparable for water and some specified oil (or other organic liquid). The nature of the 'oil' phase is most important and, often, results with one 'oil' cannot be translated directly to apply to any other 'oil.' Again, time elapsing after emulsification, temperature, *p*H value, the presence or absence of air during emulsification, and other factors play decided *rôles* in what must be the criterion of emulsifying efficiency, the *stability* of the emulsion.

We agree with King [2] that the strength and compactness of the interfacial film is the most important single factor favouring stability, other influences being effective essentially in as far as they modify the properties of the film. "Amongst these factors, emulsifying agent concentration has perhaps been too little stressed by previous investigators. It appears, for instance, that, with a sufficiently high concentration of the agent, the electrical behaviour of the emulsion will bear an insignificant relation to its stability."

Moore and Krumbholz [3] have published a note on "the relative power of various forms of protein in conserving emulsions." Preparing olive oil-in-water emulsions, they found the following proteins to possess emulsifying efficiencies in the ascending order: albumose, blood serum, white of egg, acid albumin and alkali albumin. The albumose was practically ineffective, blood serum and white of egg were only poor emulsifiers, whilst the two albumins were very effective. The results obtained, however, were only of a qualitative nature.

According to Krantz and Gordon [4] the size of globules of vegetable and mineral oils in emulsions stabilised with gum acacia is smaller and far more uniform than in similar emulsions using gum tragacanth. Acacia emulsions were stable over the *p*H range 2–10, the tragacanth emulsions over the range *p*H 1·9–2·3.

Clark and Mann [5] have studied the emulsifying efficiencies of sucrose, dextrin, starch, gum arabic, and egg albumin. Emulsions of benzene and of kerosene were made in aqueous solutons of the emulsifying agents at various concentrations. In each instance the oil phase was 75 per cent. of the total volume. After seven weeks the emulsions were graded on a scale of ten as regards stability, *i.e.*, efficiency of the emulsifying agents.

Thus, using 1 per cent. solutions of the emulsifiers and dispersing benzene therein, the following gradation was given: egg albumin, 10; starch, 6; gum arabic, 5; dextrin, 3; sucrose, 0. When kerosene was emulsified, the gradation appeared as: egg albumin, 10; starch, 9; gum arabic, 3; dextrin, 2; sucrose, 2.

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[1] See Smith, *J. Soc. Chem. Ind.*, **47**, 345 T (1927); Cohan and Hackerman, *Ind. Eng. Chem. Anal. Edn.*, **12**, 210 (1940).

[2] *Trans. Faraday Soc.*, **37**, 168 (1941).

[3] *Proc. Physiol. Soc., London*, **54**, 22 (1898). Very similar observations have also been made by Fischer and Hooker, "Fats and Fatty Degenerations" (1917), p. 32.

[4] *J. Am. Pharm. Assocn.*, **15**, 93 (1926).

[5] *J. Biol. Chem.*, **52**, 160 (1922).

The presence of electrolytes influenced the emulsifying efficiencies, but egg albumin still stood out as the most effective emulsifier, and the emulsions still received 10 points on the arbitrary scale, when HCl, NaI, NaOH, $NaHCO_3$, or Na_2SO_4 were present in the continuous phase.

Marshall[1] carried out some experiments on emulsifying power, and found that whilst 1 grm. of gum acacia in 4 c.c. water will emulsify 21 c.c. of almond oil, 1 grm. of soft soap in 4 c.c. water will emulsify 210 c.c. of almond oil. A solution of 0·2 grm. of saponin in 4 c.c. of water could emulsify 90 c.c. of almond oil. Marshall then determined the quantities of various emulsifiers and water required to emulsify 200 c.c. of almond oil. The experiments were carried out at 13° C., the method employed being the pharmaceutical one of trituration in a mortar. The quantities required were: gum acacia, 10 grm. in 23 c.c. water; soft soap, 1 grm. in 3·8 c.c. water; saponin, 0·2 grm. in 9·6 c.c. water; condensed milk, 5 grm. in 20 c.c. water.

Crockett and Oesper,[2] and also Hiss,[3] have qualitatively found that gum tragacanth is much inferior to gum acacia for preparing pharmaceutical emulsions, whereas Krantz and Gordon[4] required 0·5 grm. tragacanth and 2·5 grm. acacia in preparing 25 per cent. emulsions of cotton-seed oil of "Nujol" in water. The average diameter of the oil globules, however, was very much smaller in the acacia prepared emulsions, thus pointing to better emulsification. Briggs and Schmidt[5] have mentioned that for emulsifying benzene in water 1 per cent. gum arabic solution is inferior to 1 per cent. gelatin solution, this in turn being much inferior to the alkali soaps.

Pickering[6] graded "good" emulsifiers of mineral oils in water as follows: Soft soap is the most effective. "Dissolved starch, milk and flour are good, though the latter forms a flocculent and not a creamy emulsion. Milk gives rise to solid clots. Glue emulsifies well and so does egg albumin, but the emulsion with the latter is rather frothy owing to enclosed air bubbles. Saponin and quillaia bark give good emulsions when the proportion of oil present is not large."

The emulsifying efficiencies of the sodium salts of the paraffin series of fatty acids have been studied by Donnan and Potts,[7] using a pure hydrocarbon oil and water. Only the higher members of the series, from sodium laurate onwards, acted as emulsifying agents. Donnan and Potts connected this fact with the colloidal nature of the solutions of the higher soaps.

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[1] *Pharm. J.*, **28**, 257 (1909).
[2] *Ind. Eng. Chem.*, **9**, 967 (1917).
[3] *Bull. Pharm.*, **13**, 229 (1899).
[4] *J. Am. Pharm. Assocn.*, **15**, 83 (1926).
[5] *J. Phys. Chem.*, **19**, 484 (1915).
[6] *J. Chem. Soc.*, **91**, 2002 (1907).
[7] *Kolloid-Z.*, **7**, 208 (1910).

Briggs and Schmidt[1] observed that sodium resinate (pure resin soap) was not so efficient as sodium oleate for emulsifying benzene in water. White and Marden[2] investigated the emulsifying capacities of sodium stearate and sodium palmitate for preparing emulsions of kerosene and linseed oil in water, correlating the results from the values for the surface tensions of the soap solutions. No very definite data on emulsifying efficiencies were obtained.

On the other hand, Yajnik and Ilahi[3] found that sodium palmitate was more efficient than sodium stearate for emulsifying vegetable oils in water, and they connect the fact with the further observation that solutions of sodium palmitate have a lower surface tension than solutions of sodium stearate. However, their method of preparing the emulsions is, in the present writer's opinion, open to question, and no study was made of the degree of dispersion attained. More reliable quantitative work by Stamm concerned the dispersion of 5 per cent. benzene in 0·0005 N solutions of sodium, potassium and caesium palmitate. Size-distribution curves showed these different monovalent soaps to give the same mass maxima and the same total surface of dispersed globules. The free fatty acids, *e.g.*, palmitic acid, are decidedly inferior to the soaps as emulsifiers.

Woodman[4] observed that potassium oleate is more efficient than sodium oleate in emulsifying 10 c.c. toluene in 10 c.c. aqueous 0·4 per cent. solution. Again, gelatin was better than sodium oleate for dispersing 20 c.c. toluene in 10 c.c. of the aqueous solution. Both investigations were quantitative, inasmuch as the number of shakes required by Briggs' method was determined. Mead and McCoy[5] observed that sodium oleate is a more efficient emulsifier than sodium stearate.

According to Kremnev,[6] who emulsified benzene in aqueous solutions of alkali oleates, the emulsifying power decreases in the order Li, Na, K and depends on the dispersion of the soap, being highest with 0·016 N solutions, when an unsaturated monolayer covers the benzene globules.

INVESTIGATIONS BY KING

Important investigations have been made by King and his collaborators under the general heading of the stability of emulsions.

In the first paper by King and Mukherjee[7] soap-stabilised emulsions are investigated. Size-frequency analyses enabled more precise data than had hitherto been reported by earlier workers.

Rightly emphasising that "the efficiency of an emulsifying agent is a very specific property" and that "a soap may give an excellent emulsion with one liquid and an inferior emulsion with another," the authors describe results on emulsions of kerosene and olive oil in water. The time factor was followed by size-frequency analyses. In addition to stability measurements experiments were made to determine the effect of varying the amount of emulsifying agent, the mechanical method adopted for dispersion, heat, $CaCl_2$, and acid on the stability.

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[1] *Loc. cit.*

[2] *J. Phys. Chem.*, **24**, 617 (1920).

[3] *Kolloid-Z.*, **37**, 139 (1925).

[4] *J. Pomology Hort. Sci.*, **4**, 102 (1925).

[5] *Colloid Symposium Monograph*, **4**, 50 (1926).

[6] *Acta Physicochim. U.R.S.S.*, **2**, 779 (1935).

[7] *J. Soc. Chem. Ind.*, **58**, 243 (1939).

Table 14 is reproduced from King and Mukherjee's paper. The suffix refers to the length of time in days which elapsed between emulsification and analysis.

Dealing with the relative emulsifying efficiencies of various soaps it is stated that : " It will be seen that sodium and potassium soaps produce emulsions of very similar stability, the potassium soaps being slightly more efficient except in a few of the olive oil emulsions. On the other hand, the ammonium soaps are much inferior to those of the other two metals. Of the three fatty acids used, the soaps of oleic acid are the most efficient emulsifiers, followed rather closely by the stearate soaps ; palmitates give rather unstable emulsions. There is ample evidence to generalise as above, and it will be seen that the methods used to produce the emulsions have little effect on the relative stabilities due to the different soaps. The most efficient agent is potassium oleate, which produced a kerosene emulsion of stability 44·6 (13) ; the least efficient is ammonium palmitate, which gave a value of 19·7 (24). The general behaviour of emulsions stabilised by different soaps is strikingly similar."

The authors do not concur that the quality of an emulsion is predicted by the size-frequency distribution of the globules, since this affords little clue to the separation of free oil or the length of life of the emulsion. Not the area of interface, but *change in the area of interface with time*, is the criterion for emulsion stability. Table 15 shows this.

King and Mukherjee[1] next reported on the stability of emulsions containing hydrophilic colloids which are characterised by their high degree of hydration, tendency to gel formation, and the formation of viscous aqueous dispersions. Interfacial adsorption of such colloids would be expected to yield films quite different to those by soaps, particularly where the influence of added salts is concerned.

The complete table of results should be consulted. The authors' summary states that : " The present investigation shows that emulsions stabilised by hydrophilic colloids are, on the whole, less fine but more stable than the corresponding soap-stabilised systems ; they are also rather less influenced by addition of electrolyte and rise of temperature. The difference in behaviour between the various members of the group is both marked and significant. In general, those agents which form very viscous dispersions or even gels at ordinary temperatures promote emulsions which may be coarse but are usually extremely stable. Variation in conditions leading to decreasing viscosity of dispersion or to gel-sol transformation results in immediate deterioration of the emulsion. This is clearly illustrated by the agar system, which forms excellent emulsions as long as there is the possibility of gelation, but at higher temperatures where this is prevented, no stable emulsion can be formed.

Emulsifying agents of the hydrophilic colloid type, which form only

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[1] *J. Soc. Chem. Ind.*, **59**, 185 (1940).

TABLE 14

PERCENTAGE DISTRIBUTION OF OIL DROPLETS OF DIFFERENT SIZE IN HOMOGENISED OLIVE OIL EMULSIONS

No.	2^{0}	2^{4}	2^{7}	2^{10}	2^{14}	2^{21}	2^{30}	4^{0}	4^{4}	4^{7}	4^{10}	4^{14}	4^{21}	4^{30}	9^{0}	9^{4}	9^{7}	9^{10}	9^{14}	9^{30}	37*	39^{0}	39^{7}
Mean dia. meter (μ.)																							
0·5	62·2	57·3	51·1	38·9	30·5	25·6	21·0	48·5	42·6	38·1	28·6	22·5	18·6	13·5	37·9	30·4	23·2	18·1	12·1	7·9	26·8	30·3	23·9
1·5	25·3	27·4	30·4	36·2	38·8	38·4	37·6	31·1	33·1	34·2	35·9	40·1	34·0	33·9	35·7	39·1	40·9	40·4	35·7	34·7	41·2	41·8	41·0
2·5	8·2	9·9	11·8	14·2	18·2	20·7	22·0	12·8	14·5	15·9	19·3	20·4	27·2	27·2	17·2	17·7	21·0	23·2	29·5	32·1	12·5	11·3	21·1
3·5	3·2	3·8	4·4	6·8	7·7	9·6	11·3	4·2	5·8	7·2	8·8	9·5	10·0	12·2	5·3	6·8	7·0	9·9	13·0	13·0	7·9	7·9	5·9
4·5	1·1	1·6	2·0	3·5	4·0	4·5	5·6	3·1	3·5	3·9	5·6	5·5	7·2	8·8	3·2	4·7	5·5	5·9	6·6	7·7	9·4	6·1	5·9
7·5	—	—	0·3	0·4	0·8	1·2	2·0	0·3	0·5	0·7	1·8	1·5	1·8	2·6	0·7	1·3	1·9	1·7	2·0	2·8	2·6	0·8	1·6
12·5	—	—	—	—	—	—	0·5	—	—	—	—	0·5	1·1	1·1	—	—	0·5	0·6	0·8	1·2	0·5	0·6	0·6
20	—	—	—	—	—	—	—	—	—	—	—	—	—	0·6	—	—	—	0·2	0·3	0·6	0·3	—	—
Free oil	—	—	—	—	—	6·25	22·5	—	—	—	—	6·2	12·5	37	—	—	—	2·5	18·7	50	6·2	—	31
Agent	Potassium oleate							Sodium stearate							Ammonium palmitate						Na oleate	Na oleate + CaCl^{2}	

* Emulsion exposed to a temperature of 85°

TABLE 15

Variation of area of interface of emulsions of olive oil in water produced by soap formation in situ
(all values × 10^3)

No.	Time of keeping (days) Agent	0	4	7	10	14	21	30	t^* (days)	ξ
1	Sodium oleate	23·29	22·42	21·39	19·72	18·01 (0·0)	12·5 (10)	7·74 (18·7)	23	44·9
2	Potassium oleate	26·38	25·21	22·04	20·69	19·36 (0·0)	16·41 (6·2)	10·34 (22·5)	26	49·3
3	Ammonium oleate	21·9	19·65	14·91	13·74 (6·2)	12·07 (10)	8·91 (25)	4·92 (37·5)	16	38·6
4	Sodium stearate	21·34	20·19	19·36	15·77	12·66 (6·2)	9·61 (12·5)	5·15 (31)	18	39·5
5	Potassium stearate	21·69	19·84		17·82	13·26 (6·2)	7·65 (12·5)	5·73 (27·5)	17	32·5
6	Ammonium stearate	19·65	18·61	13·23	11·0 (6·2)	7·91 (18·7)	5·83 (30)	4·12 (37·5)	12	23·4
7	Sodium palmitate	19·51	17·42	13·58	12·72	10·58 (10)	5·79 (18·7)	4·58 (35)	15	29·9
8	Potassium palmitate	21·68	20·09	15·09	12·0	11·16 (20)	6·02 (25)	4·6 (37·5)	14	29·1
9	Ammonium palmitate	19·48	16·84	13·13	9·68 (2·5)	6·79 (18·7)		3·78 (50)	10	21·5

* Time of half break

Variation of area of interface of homogenised, soap-stabilised kerosene emulsions ; (a) soap added to aqueous phase, (b) soap formed by reaction in situ
(all values × 10^3)

No.	Time of keeping (days) Agent		0	7	14	21	30	ξ
10	Sodium oleate	*a*	27·4	25·7	20·42 (0·0)	16·27 (3·7)	7·42 (15)	41·1
11	Sodium oleate	*b*	30·73	25·92	24·03 (0·0)	18·46 (0·0)	9·64 (6.2)	43·5
12	Potassium oleate	*a*	28·08	25·65	22·95 (0·0)	17·76 (2·5)	8·79 (12·5)	43·7
13	Potassium oleate	*b*	33·2	28·02	24·58 (2·5)	21·07 (6·2)	10·86 (15)	44·6
14	Sodium stearate	*a*	24·42	23·74	16·63 (0·0)	14·27 (10)	6·63 (35)	41·0
15	Sodium stearate	*b*	27·53	23·89	20·12 (7·5)	14·94 (7·5)	7·18 (18·7)	42·9
16	Potassium stearate	*a*	24·61	23·84 (2·5)	17·52 (17·5)	15·25 (31)	6·6 (56)	41·0
17	Potassium stearate	*b*	27·65	25·02	21·41 (0·0)		8·37 (15)	42·9
18	Sodium palmitate	*a*	23·9	18·61	15·8 (7·5)	10·91 (18·7)	5·26 (31)	38·4
19	Sodium palmitate	*b*	25·92	24·05	16·51 (5.0)	12·39 (10)	4·44 (50)	39·9
20	Potassium palmitate	*a*	23·6	20·67	17·12 (6·2)	12·0 (18·7)	5·85 (31)	39·8
21	Potassium palmitate	*b*	27·2	24·84		16·9 (5.0)	4·77 (44)	40·3
22	Ammonium oleate	*b*	26·33	20·66 (10)		11·91 (25)	6·42 (50)	39·7
23	Ammonium stearate	*b*	26·53	19·11 (3·7)	11·84 6·2)		4·38 (42)	35·9
24	Ammonium palmitate	*b*	25·52		7·36 (50)	2·0 (75)	completely broken	19·7

The figures in parentheses indicate the percentage of the total oil volume which has separated as a free layer in each case. The direct measure of emulsion stability is given by ξ which is the reciprocal of the instability factor (ds/dt), the rate of decrease of each square centimetre of fresh emulsion interface per day.

mobile suspensions, produce emulsions which are often very fine in the initial stages but coarsen very rapidly.

All these results support the hypothesis that the efficiency of the emulsifying agent is due to its power of forming a solvated membrane of considerable strength at the oil/water interface. Those agents which gel readily are capable of forming such membranes and hence produce stable emulsions. In some systems, and especially those of the gums the emulsions themselves have a high viscosity, which means that there is a considerable quantity of agent in the dispersion medium and not adsorbed at the interface. This makes the mechanical break-up of the oil droplets difficult and leads to the formation of coarse emulsions; such viscosity, however, is also a factor favouring stability since both creaming and coalescence due to kinetic impact are minimised.

Hydrophilic agents with little tendency to gelation produce initially fine emulsions owing to the low viscosity of the continuous phase, but such emulsions are relatively unstable because not only are solvated membranes absent but also there will be less tendency than with the soap type of molecule to form an oriented adsorbed layer."

THE EMULSIFIABILITY OF OILS IN WATER

With a given emulsifying agent and water, it is theoretically possible that different oils will be capable of being emulsified to different extents. Very little quantitative work, however, has been carried out in this connection. Clayton[1] investigated the emulsifiability of certain edible oils and fats in water at various temperatures, using the Donnan drop-number method. Very little difference indeed was found in the drop-numbers of seven common oils and fats; the temperature effect was negligible.

Meunier and Maury[2] investigated the emulsifiability of several oils in water by the drop-number method. The following figures were obtained at 21° C.:—

Neat's-foot oil . . . . . . = 18 drops.
Olive oil . . . . = 20 ,,
Linseed oil . . . . = 18 ,,
Castor oil . . . . = 9 ,,
Mineral oil (D = 0·934) . . . . = 9 ,,

The first three oils are thus about twice as easily emulsified in water than is castor oil or mineral oil. They found that temperature had practically no influence on the drop-number.

Mészáros[3] placed in a 100-c.c. flask 80 c.c. of water and 8 grm. of edible fat at 40° C., followed by 60 minutes' shaking mechanically. The resulting emulsion was kept in a separating funnel for 24 hours at room temperature. The tubidity and fat content were then determined in 30 c.c. of the aqueous liquid. The results were expressed in terms of the emulsifiability number (E–Zahlen), *i.e.*, the milligrams of fat which is emulsified in 100 grm. of water *without the aid of an emulsifying agent.*

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[1] *Trans. Faraday Soc.*, **16**, Appendix 24 (1921).
[2] *Collegium*, **1910**, 227, 285.
[3] *Z. Untersuch. Lebensm.*, **69**, 318 (1935).

Four groups of fats were noted on this basis, probably related to the molecular structure of the fats. Class I showed very good emulsifiability, the value of E–Z. being over 50. They are goose fat, horse fat, lard, and raw rape oil. Class II, with good emulsifiability (E–Z. = 20 to 50), included butter-fat, arachis oil, and sesame oil. In class III, characterised by poor emulsifiability (E–Z. = about 10), were coco-nut oil, palm kernel oil, soya bean oil, and beef tallow. Class IV showed very poor emulsifiability (E–Z. = below 10) and included illipé butter and hardened blubber.

The modern view of emulsions, considered from the Langmuir-Harkins' theory of orientation, is that oils and fats of animal or vegetable nature, being mixed glycerides, should have similar emulsifiabilities in water or soap solutions. Mineral oils should be less readily emulsified in water, since they do not possess caroxylic or other groupings with an affinity for water. In any case, the question of emulsifiability in water only is of minor importance, and is only investigated as a necessary preliminary to further work or emulsification in water containing emulsifying agents, these being necessary for all emulsions other than very dilute. Engineers, however, have been concerned with the question of the emulsification of the oil in forced-feed lubrication, and various tests have been devised to ascertain the extent to which a given lubricating oil will emulsify in water. Thus Herschel's [1] test is as follows : " One part of oil to two parts of water are stirred for five minutes in an ordinary 100 c.c. graduated cylinder at a specified speed and temperature by means of a flat, metal paddle. The emulsion thus formed is allowed to stand at the same temperature, and readings are taken at intervals of the volume of oil separated out. The maximum rate of settling, ascertained from a table, is called the 'demulsibility,' and is used as a measure of the resistance of the oil to emulsification."

The " demulsibility " of lubricating oils for use in steam turbines has also been studied by Philip,[2] Delbridge,[3] and Conradson.[4] Further, Dimmig [5] has elaborated a method of measuring the emulsifying tendency of lubricating oils based on interfacial tension of determinations.

Using a drop-pipette (see p. 460), a comparison of the interfacial tensions of the various oils against water and 0·01 N.NaOH is obtained by counting the number of drops formed by a determined volume of the oil issuing slowly from the top of a calibrated pipette, immersed in the liquid. A factor K is then obtained, viz. :—

$$K = \frac{\text{volume of 100 drops of oil in 0·01N.NaOH}}{\text{volume of 100 drops of oil in distilled water}}.$$

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[1] *Proc. Amer. Soc. Testing Materials*, **16** (part 2), 248—65 (1916); also U.S. Bur. Standards, *Tech. Papers*, No. **86**, pp. 1—37 (1917); cf. Bowles, *Proc. Am. Soc. Testing Materials*, **26**, (part 1), 370—80 (1926).

[2] *J. Soc. Chem. Ind.*, **34**, 697 (1915).

[3] *Proc. Am. Soc. Testing Materials*, **20**, (part 1), 416—26 (1920).

[4] *Ibid.*, **16** (part 2), 273—80 (1916); van Rysselberge, *Bull. fédération ind. chim. Belg.*, **7**, 445 (1929); Kvartin and Ovchinnikova, *Chem. Abs.*, **35**, 1613 (1941).

[5] *Proc. Am. Soc. Testing Materials*, **23**, 363—73 (1923).

Since the size of an oil drop is approximately proportional to the value of the interfacial tension, it follows that the closer K approaches unity, the less is the tendency for the oil to become emulsified. Values of K between 0·75 and 1 are considered satisfactory; values of K less than 0·75 indicate the possibility of emulsification. The method is an advance on the older methods. Provided close attention is paid to (i) the use of an accurately ground tip of standard internal radius (0·5 mm.), (ii) slow delivery of the oil as drops, (iii) temperature, reproducible results should be possible in the hands of different workers.

Leaving the question of the emulsifiability of oils in water, and considering water containing an emulsifying agent, the only investigation made has been on the emulsification of vegetable oils in soap solutions.

Lehner and Bishop[1] determined the emulsifiability of eight oils in sodium oleate solutions at 100° C. Plotting their results with "per cent. by volume of oil emulsified" as ordinates, and the "minimum amount of sodium oleate" emulsifier required as abscissæ, closely similar curves were obtained with cotton-seed, maize, linseed, olive, rape, arachis, sesame and castor oils, showing that they were all emulsified to about the same extent.

SPECIFICITY IN EMULSIFICATION

On the basis of the orientation of the emulsifying agent in the interface between oil and water (using "oil" as a generic term for organic liquids), it is to be expected that specificity will be exhibited in the preparation of emulsions. The work of Pick[2] on margarine emulsions suggests that the nature of the oil or fat is itself an important factor in determining the stability of the W/O emulsion. By determining the electrical breakdown of such emulsions, he observed that hydrogenated fish oils emulsify water best. Again Tartar and his co-workers[3] in a study of the emulsification of benzene, toluene, xylene, aniline, orthotoluidine, nitrobenzene and dimethylaniline in water containing soaps state that their data indicate "that methyl groups attached to the benzene ring have a beneficial effect on the emulsifiability of the 'oil.' The amino group, however, seemed to exert an inhibitory influence. Two methyl groups, as in the case of dimethylaniline, seemed to overcome this inhibitory influence of the amino group and emulsification took place readily. When two different substituent groups were attached to the benzene ring, as in orthotoluidine, influence of the amino group seemed to dominate and the 'oil' did not readily emulsify. The nitro group favoured emulsification."

Kernot and Knaggs[4] also demonstrate the specific influence of the oil. Using gelatin to emulsify oils, they concluded that emulsification was easier with oils containing active groups, such as double or triple linkings. Thus, gelatin from calf-skin treated with NaOH, whilst a very poor emulsifying agent for liquid paraffin or soya bean oil, is very efficient with cod-liver oil or shark-liver oil.

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[1] *J. Phys. Chem.*, **22**, 68 (1918).
[2] *Allgem. Öl-Fettztg.*, **26**, 577 (1929).
[3] *J. Phys. Chem.*, **33**, 446 (1929).
[4] *J. Soc. Chem. Ind.*, **47**, 96 T. (1928).

Woodman and Taylor [1] have shown that in emulsions prepared with the aid of bentonite, marked specificity of the oil is observed. Again, investigating surface-active dyes, Rehbinder and Wenström [2] noted marked specific effect. For example, picric acid would not emulsify benzene in water, although it stabilised mercury emulsions. The highly surface-active Twitchell reagent shows marked differences in its capacity to emulsify various oils.[3]

Moeller [4] has shown that aqueous suspensions of lanthanum hydroxide will promote emulsions with some organic liquids but not with others (see p. 142).[5] King has also dealt with this problem and given a table of order of ease of emulsification for several organic liquids.

MIXED EMULSIFYING AGENTS

Only in limited instances do technical emulsions contain a single emulsifying agent. For reasons depending on flavour or viscosity, several colloid ingredients may be present. Empiricism is apparent in this connection and research is needed on the relative extents of adsorption at a dineric interface of the colloids in a mixture of emulsifying agents, as well as a study of the type and strength of the adsorbed film. Usually a colloid such as a gum is employed solely to increase the viscosity of the continuous phase, thus imposing a mechanical restraint on the sedimentation of the disperse phase, but its possible influence on the character of the interfacial film should not be overlooked.

Some interesting results regarding mixed emulsifying agents in the preparation of pharmaceutical emulsions were obtained by Smith and Hazley.[6] A mixture of gum acacia and gum tragacanth proved more efficient than either gum alone. Gum acacia gave good emulsions, but their low viscosity permitted creaming. Gum tragacanth gave coarse emulsions which did not break, as the mucilage possessed a high viscosity. Hence, in the mixture of gums, the excellent dispersive properties of gum acacia are aided by the mechanical resistance to creaming imposed by the presence of gum tragacanth. When apple pectin was used with gum acacia, the emulsions showed clear water separation below on standing. This is considered to be due to the setting of the pectin to a gel and subsequent syneresis. Similarly, a mixture of pectin and agar gave emulsions which creamed rapidly.

Pectin is recommended in mayonnaise of the American (concentrated) type, in order to prevent separation of the emulsion due to freezing, which induces in ordinary mayonnaise a change in the egg proteins. Different results might follow the use of other colloids of varying degrees of hydration capacity.

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[1] *J. Soc. Chem. Ind.*, **48**, 121 T. (1929).

[2] *Kolloid-Z.*, **53**, 147 (1930).

[3] Nishizawa and Inoue, *Kolloid-Z.*, **58**, 225 (1932).

[4] *J. Phys. Chem.*, **44**, 259 (1940).

[5] *Trans. Faraday Soc.*, **37**, 176 (1941).

[6] *Quart. J. Pharm. Pharmacol.*, **3**, 362 (1930). See similar results results by King and Mukherjee, *J. Soc. Chem. Ind.*, **59**, 185 (1940).

That the subject of mixed emulsifiers merits a full investigation is evident in recalling the peculiar creaming effects of colloids when added to milk or rubber latex. Again, the recent work on coacervation is suggestive.

FINELY-DIVIDED SOLIDS AS EMULSIFIERS

Finely-divided solids in certain instances may promote emulsification of oils in water or of water in oil. Thus a North African argillaceous earth readily emulsifies oils in water, and can be used as a substitute for soap.[1] The first extensive survey of insoluble emulsifiers, however, was made by Pickering,[2] who found that the basic sulphates of iron, copper, nickel, zinc and aluminium act as efficient emulsifying agents for dispersing mineral oil in water. Other useful emulsifiers were freshly-precipitated calcium carbonate and arsenate, lead arsenate, and various unheated fine clays. Unstable quasi-emulsions were promoted by lime, silica, dried alumina or plaster of Paris; also by freshly-precipiated basic cadmium sulphate, magnesium hydroxide, copper hydroxide, tin oxychloride, and the sulphides of iron and copper. Pickering[3] believed that emulsification depended on the size of the particles constituting the emulsifier, and that the size of the emulsion globules varied directly with the size of the particles of the emulsifying agent.[4] He also pointed out the perfectly correct condition that for emulsions of oil in water the finely-divided emulsifying agent must be more readily wetted by water than by oil.

Briggs and Schmidt[5] found that hydrous ferric oxide in aqueous suspension is a "fairly good" emulsifier for benzene. Later, Briggs[6] showed that hydrous ferric oxide, arsenious sulphide, and finely-powdered silica promote emulsions of benzene and kerosene in water. On the other hand, carbon black and mercuric iodide promote the emulsification of water in benzene or kerosene.

Schlaepfer[7] in 1918 formulated that "insoluble particles, which are more easily moistened by oil than by water, will have a tendency to facilitate the emulsification of water in oil." He found that 70 per cent. by volume of water could be dispersed in 30 per cent. by volume of kerosene, using 1 grm. of carbon (best American soot), giving a very viscous emulsion, stable for at least a week. It was found impossible to obtain an emulsion of kerosene in water with the aid of carbon. These results were confirmed by Moore,[8] who studied the emulsification of water and of aqueous solutions of ammonium chloride in kerosene. He found (1) that, on the whole, the larger the amount of carbon (lampblack) used, the smaller were the diameters of the emulsified water globules; (2) if the volume of kerosene be kept constant, the average diameters of the emulsified globules increase as the total volume of the liquids increases. The more concentrated emulsions, particularly with 50 per cent. by volume of normal NH_4Cl dispersed therein, were firm and stiff, of a buttery consistency, and very stable. To make 30 c.c. of such an emulsion required the presence of 0·5 grm. of lamp-black.

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[1] *Pharm. J.*, **6**, 1228 (1898).

[2] *J. Chem. Soc.*, **91**, 2001 (1907).

[3] *J. Soc. Chem. Ind.*, **29**, 129 (1910).

[4] In this connection reference should be made to Alexander's interesting paper on "The Zone of Maximum Colloidality," *J. Am. Chem. Soc.*, **43**, 434 (1921).

[5] *J. Phys. Chem.*, **19**, 484 (1915).

[6] *Ind. Eng. Chem.*, **13**, 1008 (1921).

[7] *J. Chem. Soc.*, **113**, 522 (1918). See Sata, *Kolloid-Z.*, **81**, 184 (1937).

[8] *J. Am. Chem. Soc.*, **41**, 940 (1919).

Similarly, Odell,[1] studying the effect of different amounts of carbon black on the formation of stable emulsions of motor fuel and water (30 : 70) observed that as the amount of carbon was increased to 5·7 per cent. of the oil used, the dispersed water globules were progressively smaller and the emulsions more permanent. Too much carbon was undesirable, the optimum amount being between 5·7 and 12 per cent. of the oil used.

Briggs [2] showed that certain finely-divided solids, when used together, could exert antagonistic emulsifying effects. For example, if to 0·8 grm. of carbon black, normally capable of promoting the dispersion of 25 c.c. of water in 15 c.c. kerosene, one added 0·1 grm. of silica (350 mesh), no emulsion was possible. On the other hand, kerosene can be emulsified in a water suspension of silica, but if sufficient carbon black be present, no emulsion can be made.[3] Similarly, 1 part of mercuric iodide in 20 parts of silica will prevent the latter from emulsifying 25 c.c. of kerosene in 25 c.c. of water. Again, alumina is able to " break " emulsions stabilised by carbon.[4]

So far no work has been done on the possible antagonistic effects of finely-divided solids and substances in colloidal solution, such as soaps or gelatin, though the results would have theoretical significance.

Colloidal clay as an efficient emulsifying agent for oil and fats has been investigated by Weston.[5] According to him, however, colloidal clay is capable of facilitating the emulsification of oil in water or of water in oil.[6] Such a result certainly required further investigation in view of the opinion that a given emulsifying agent only promotes *one* type of emulsion with any two given liquids to be emulsified.

Woodman [7] undertook such investigation and showed that Weston's claim was correct. Various clays and derivatives prepared therefrom by base exchange and hydrolysis promoted mainly dual emulsions, O/W and W/O types, with fatty acids, fixed oils containing free fatty acids, and with phenols and hydrogenated phenols. " The hypothesis advanced is that this is due to chemical interaction of the fatty acids, *etc.*, with sodium and calcium hydroxides, *etc.*, obtained by hydrolysis of the clay when in aqueous suspension, or with breakdown products of the clay itself. The original emulsifier thus undergoes change, and soaps are introduced into the system. The changes taking place in the original emulsifier and the different emulsifiers present can easily be made to afford sufficient explanation of the fact that dual types are formed ; the clays, *as such*, are not responsible, and the results are brought strictly into line with the usual emulsion theory as enunciated by Clayton that one emulsifier cannot promote two types of emulsions with any two given liquids to be emulsified."

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[1] U.S. Bur. Mines, *Tech. Paper*, **304**, 36 (1923).

[2] *Ind. Eng. Chem.*, **13**, 1008 (1921).

[3] Silica binds water more strongly than does carbon. Culbertson and Winter, *J. Am. Chem. Soc.*, **63**, 95 (1941).

[4] Odell, *loc. cit.*, p. 41.

[5] *Chem. Age* (*London*), **4**, 604, 638 (1921).

[6] *Loc. cit.*, p. 640.

[7] *J. Phys. Chem.*, **34**, 299 (1930).

Kieselguhr has been used by Lapworth and Pearson [1] as an emulsifying agent when studying the reduction of emulsified nitro-compounds. Sheppard [2] used salts of low solubility, *e.g.*, $PbSO_4$, for emulsifying nitrobenzene in mineral acids.

Bhatnagar [3] used such precipitates as zinc hydroxide, aluminium hydroxide and lead oxide for making emulsions of the water-in-oil type.

An extensive investigation on the use of finely-divided solids as emulsifiers has been carried out by Bechold, Dede, and Reiner.[4] They found that the formation of emulsions depends upon : (1) The grain size of the powder. The smaller the grain the better is the emulsion, until an optimum is reached, after which smaller grains have inferior emulsifying properties. (2) The quantity of powder. The more powder there is available the more globules there can be covered, providing the powder is sufficiently fine.

The solids investigated were zinc dust, iron powder, clay, kieselguhr and yeast, and they were found to be as efficient as hæmoglobin or egg-albumin solutions for emulsifying benzene, paraffin oil, nitrobenzene, aniline, isobutylaldehyde, carbon disulphide, and several organic liquids, in water.

Bancroft's theory of adsorbed films as essential for stable concentrated emulsions (see p. 199) has been extended to finely-divided solids as emulsifiers. The work of Des Coudres and Hofmann (see p. 217) leads to the conclusion that, for a solid to remain in the water phase, it must be wetted only by water ; for it to remain in the non-aqueous liquid, it must be wetted only by that liquid. It will remain in the interface between the two liquids when it is partially wetted by each. Bancroft [5] prefers an alternative explanation, viz. : "When shaken with water and a non-miscible organic liquid, solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid ; they tend to go into the other liquid phase if they adsorb the organic liquid to the practical exclusion of the water ; and they tend to pass into the dineric interface in case they adsorb the two liquids simultaneously."

Measurements of the Plateau interfacial viscosity in the case of emulsions stabilised by solid particles have been reported by Smith,[6] who found in some instances considerable increases in the viscosity as compared with the liquid/liquid interface alone. His interesting paper, however, must be regarded as quite preliminary ; for instance, the influence of particle size was not investigated. Again, the interfacial viscosity should be related to the angle of contact or to the preferential wetting of the solid.

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[1] *J. Chem. Soc.*, **119**, 765 (1921).
[2] *J. Phys. Chem.*, **23**, 634 (1919).
[3] *J. Chem. Soc.*, **119**, 1760 (1921).
[4] *Kolloid-Z.*, **28**, 6 (1921).
[5] *J. Phys. Chem.*, **19**, 287 and 308 (1915).
[6] *Phil. Mag.*, **4**, 820 (1927).

A general survey of solid emulsifying agents with special reference to the hydrous oxides and hydroxides has been made by Bennister, King and Thomas,[1] who form the opinion that few solids are sufficiently useful for technical application.

Preliminary study was made of the emulsifying properties of a number of insoluble inorganic precipitates such as calcium and barium carbonates, barium sulphate, lead sulphate, calcium phosphate, bismuth oxychloride, etc., as well as of hydrous oxides and hydroxides. In practically every case emulsions were formed, but, except with the gelatinous oxides and hydroxides. these were of such a low stability as to be of no practical importance. It was noticed that the moist precipitates were always better emulsifiers than the corresponding dry powders, which formed only quasi-emulsions in the majority of cases. Carbonates and basic salts tended to be among the most efficient of the insoluble, inorganic salt emulsifiers; thus barium carbonate formed more stable emulsions than barium sulphate, although it is difficult to give direct evaluation, since the properties of the emulsions produced varied so much with the method of preparation and, more especially, with the concentration of the reagents used in precipitation. The physical state of the solid appeared to be important, a gelatinous precipitate being usually much more efficient than a granular preparation of the same material. Thus a compact suspension of bismuth oxychloride gave what appeared to be a poor water-in-oil emulsion with kerosene or carbon tetrachloride; when, however, such a suspension had been dissolved in the minimum amount of hydrochloric acid and reprecipitated by pouring into a large volume of water, the washed precipitate gave relatively fine and stable emulsions of the oil-in-water type with both these liquids.

Emulsions prepared with all of these insoluble salts were essentially coarse and usually unstable; in nearly every case it was possible to see the adsorbed solid at the interface.

The hydrous oxides and hydroxides of eighteen elements were prepared and used to promote O/W emulsions with a hydrocarbon oil, CCl_4 and CS_2. The effect of ageing of the precipitated solids was especially investigated. Whilst it must be conceded that it is a general property of the hydrous oxides and hydroxides to promote O/W emulsions, silica gel was an exception. The other precipitates, including the amphoteric zinc and aluminium hydroxides, promoted emulsions which, although coarse, were often very stable. Smooth texture and fine subdivision are prerequisites for the solids to function well; precipitation at either very high or very low concentrations have maximum emulsifying capacity (*cf.* von Weimarn's rule). Of the alkalies used to throw down the gelatinous hydroxides, ammonia appeared best.

As regards ageing with some hydroxides no change could be noticed on ageing, while with others, notably cupric, magnesium, titanium, and zinc hydroxides, deterioration was obvious. With copper and zinc hydroxides especially, the precipitates, which were smoothly gelatinous when freshly deposited, lost their fine dispersion and became distinctly granular after a few days. This physical change might be expected to accompany the crystal growth which occurs on ageing. On the other hand, a few compounds, notably aluminium hydroxide, improved considerably in emulsifying capacity on ageing. An aluminium precipitate which was boiled for a few hours, for example, gave the best result of any of the materials examined. In this case, although transition from one type of alumina to another undoubtedly occurred, as well as crystal growth, the final product was even more gelatinous than before ageing.[1] This indicates once again the important effect of physical condition on the emulsifying properties.

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[1] *J. Soc. Chem. Ind.*, **59**, 226 (1940).

Some interesting experiments have been reported by Moeller [2] on the efficiency to promote O/W emulsions by lanthanum hydroxide. Hydrous lanthanum hydroxide was precipitated from a hot solution of lanthanum chloride with ammonium hydroxide and washed free from chloride. When an aqueous suspension of this material was shaken with benzene, toluene, xylene, mesitylene, kerosene, gasolene, and turpentine very stable emulsions resulted. However, no emulsions could be prepared with ether, isoamyl alcohol, carbon tetrachloride or chloroform. Again, it was found that when mutually flocculated by gold hydrosol, lanthanum hydroxide lost its capacity to promote emulsification.

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[1] Aged alumina is claimed by Dickeson, Fr. 838,699 (1939); Brit. 487,855 (1939); U.S. 2,194,218 (1940). The colloidal properties of hydrous alumina are treated by Larson, *Chem. Age*, **36**, 439 (1937). Alumina floc is described by Weiser, Milligan and Purcell, *Ind. Eng. Chem.*, **33**, 669 (1941). For a patent claiming alumina see Bird, U.S. 2,021,044 (1935). Heublyum, *Mfg. Perfumer*, **2**, 291 (1937) mentions alumina in soaps.

[2] *J. Phys. Chem.*, **44**, 259 (1940).

CHAPTER V

PROPERTIES OF EMULSIONS

CONCENTRATION OF EMULSIONS

When pure oil and pure water are agitated together, transient emulsions result. Apart from the oil hydrosols already described, such two-phase emulsions have but little significance. Their consideration, however, by Wa. Ostwald[1] in 1910 drew attention to the entire difference in properties of emulsions, depending on whether oil or water is the external phase. On stereometric grounds Ostwald showed that although a little oil and much water can only realise an oil-in-water system, and a little water and much oil can only realise the opposite type of emulsion, there exists a concentration range where both types of emulsion are possible. The double series of emulsions are possible only over the range 25·98 per cent. to 74·02 per cent. by volume of the internal phase.

On this theory, when to an emulsion of oil in water oil is gradually added, the distance between the globules of oil becomes less and less, until finally the globules touch and coalesce, then becoming the continuous phase, enclosing globules of water. The inversion marks a "critical point." In the same way, if water be added to an emulsion of water in oil, another critical point can be reached. Theoretically, the two critical points should coincide at 50 per cent. volume concentration provided neither liquid affects the other. In practice there is no such coincidence. Ostwald calculated that 55–72 per cent. of all possible mixtures fall in the double field.

The question of phase-volume concentration assumes major importance in technical emulsions which contain an emulsifying agent. If into a given space small spheres of the same diameter are packed as closely as possible, the volume they will occupy is 74·02 per cent. of the total available volume, and this figure is independent of the size of the spheres.[2] Each sphere touches twelve other spheres.

Very concentrated emulsions have been prepared by Pickering, when even 99 per cent. by volume of oil was emulsified in dilute soap solution. Pickering,[3] however, seemed inclined towards a volume limitation of emulsions. He called attention to the mathematical limit of 74·02 per cent. for closely-packed uniform spheres in a given space, but recognised that in emulsions the globules were not uniform and were also separated by a film of appreciable thickness. He concluded therefrom that "there does not appear to be any reason why the ratio of the volume of oil to the total volume of emulsion should be of any particular magnitude." He added, however, that in the majority of his emulsions the ratios actually found were from 65 to 82 for every 100 volumes of emulsion, and were independent of the initial proportions of oil and aqueous medium, provided the former did not exceed 80 per cent.

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[1] *Kolloid-Z.*, **6**, 103 (1910); **7**, 64 (1910); **47**, 131 (1929). *Vide* also Beijerinck, *ibid.*, **7**, 17 (1910). A related paper by Wa. Ostwald appears in *ibid.*, **32**, 77 (1923).

[2] Bouasse, "Capillarité: Phénomènes Superficiels" (Paris, 1924), p. 333; Bechold, Dede and Reiner, *Kolloid-Z.*, **28**, 18 (1921); Manegold, Hofmann and Soll, *ibid.*, **56**, 145 (1931); Manegold and von Engelhardt, *ibid.*, **63**, 12 (1933).

[3] *J. Chem. Soc.*, **91**, 2002 (1907). Zhukov and Bushmakin, *J. Russ. Phys.-Chem. Soc.*, **59**, 1061 (1927), prepared emulsions of 95 per cent. benzene in gelatin solution. See the important papers by Lester Smith, *J. Phys. Chem.*, **36**, 1401 (1932); Hartley, "Wetting and Detergency" (London, 1937), p. 153; Lawrence, *ibid.*, p. 203.

Pickering prepared stable emulsions of a mineral oil in a 1 per cent. soap solution using oil volumes of 67 per cent., 50 per cent., and 33 per cent. respectively. After standing for twelve weeks, the supernatant emulsions ("cream") were analysed at intervals from top to bottom. The average oil contents in the creams were 81 per cent., 81·9 per cent., and 77·7 per cent. respectively. The volume percentage of oil diminished throughout from the top of the column of emulsion downwards, very slowly at first and more rapidly towards the bottom. Although the *initial* oil concentrations varied greatly, the final stable emulsions were surprisingly similar in composition.

FIG. 20.—Close-packed globules in a concentrated emulsion (Morse).

Bancroft[1] has discussed the work of Ostwald and Pickering, pointing out that the globules are not all spherical and of equal size. Emulsion globules are capable of deformation of shape[2] owing to the properties of the adsorbed film of the emulsifying agent. Due to the inequality of size of the globules, the theoretical closest packing can be exceeded, small globules packing into the interstices between the larger globules. Further, coalescence does not occur when the emulsion globules touch, *i.e.*, after 74·02 per cent. by volume has been filled. The phases do not invert to yield a new continuous medium. Due to the presence of a surface film around the globules, the globules may squeeze together until a vanishingly small space separates them (cf. Fig. 20). It is now well known that dual emulsions can be prepared over any range of volume ratios. Very concentrated emulsions of both the O/W and W/O types have been discussed in the literature of this subject.

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[1] *J. Phys. Chem.*, **16**, 179 (1912).

[2] Hatschek, *Kolloid-Z.*, **7**, 71 (1910).

Woodman [1] has extended the work of Pickering. Emulsions were made of toluene, benzene and paraffin in 0·4 per cent. gelatin solution. The percentage of oil taken to the total volume of both phases varied from 0·7 to 83·3 per cent. in 34 different experiments. On standing, the emulsions "creamed," and analysis of the creams revealed that they contained on the average 72·28 per cent. by volume of the oil, the actual range being 65·5 to 80·5 per cent. The emulsions containing initially from 75 to 83·3 per cent. oil did not yield creams of greater oil content.

Similarly, Parke [2] prepared emulsions of benzene and toluene in soap solutions and found that whenever an emulsion containing more than 74 per cent. by volume of internal phase was homogenised, there always resulted a new emulsion containing approximately the volume of the internal phase required for the globules to be in closest packing, provided they had uniform diameters.

Woodman argues "that there is only one *true* emulsion which can exist permanently, the emulsion being one containing 74·048 per cent. of internal phase by volume." Less concentrated emulsions are considered as mixtures of this true emulsion and exess of external phase ; more concentrated emulsions arise because the oil globules are not uniform in size and are deformable.

Woodman's suggestion is certainly interesting and probably concerns an ideal theoretical emulsion. The present writer's experience with condenser water emulsions on the one hand and with technical emulsions on the other, the technical being of all concentrations as made in modern emulsifying machinery, leads him to the conclusion that perfectly stable (non-creaming) emulsions of *any* concentration are satisfactorily attained.

A study of inversion by the alteration of volume concentration in the case of olive oil emulsions has been made by Robertson,[3] special attention being given to "the influence of the proportion of alkali to the total volume of emulsion upon the critical ratio of water to oil at which the emulsion changed character and ceased to be an oil-in-water emulsion." Measured amounts of a very pure olive oil, containing only traces of free fatty acid, and of distilled water and NaOH, were shaken in special bottles under standard conditions. The resulting emulsions were examined under the microscope and by the use of Sudan III., an oil-soluble dye which helps to define the emulsion type.[4]

Robertson maintained the concentration of NaOH in the emulsions constant, increasing the concentration of water 1 per cent. in each succeeding experiment. He found that decreasing the proportion of water continued to give oil-in-water emulsions, until the proportion of water to oil reached a definite critical value at which the emulsion abruptly changes to the water-in-oil type. The critical ratio is defined as "the mean of the smallest ratio for which an oil-in-water emulsion can be obtained, and of the largest ratio for which a water-in-oil emulsion can be obtained." Thus, if a mixture containing 8 c.c. of water and NaOH gives an oil-in-water emulsion, whereas a mixture containing the same amount of NaOH, but 7 c.c. of water, gives the other type of emulsion, the critical ratio will be 7·5/92·5, since the total volume is constant, viz., 100 c.c. The error is, of course, 0·5/92·5. The results obtained by Robertson are typified in Table 16.

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[1] *J. Pomol. Hort. Sci.*, **4**, 184 (1925).
[2] *J. Chem. Soc.*, **1933**, 1458.
[3] *Kolloid-Z.*, **7**, 7 (1910).
[4] See p. 461.

Table 16

Phase-Volume Influence on Emulsion Type

Oil c.c.	Water c.c.	5N. Na OH. c.c.	Emulsion Characteristics.
99	0	1	Water-in-oil. Fluid. Yellow.
98	1	1	Ditto.
96	3	1	Ditto.
92	7	1	Water-in-oil. Yellow cream.
91	8	1	Water-in-oil.
90	9	1	Oil-in-water. Creamy white, very viscous.
89	10	1	Ditto.
			Critical ratio $= \frac{9 \cdot 5}{90 \cdot 5} = 0 \cdot 105$.

Throughout all the experiments 1 c.c. of NaOH solution was used, only the normality of the NaOH being varied for each series of emulsions. The results are summarised in Table 17.

Table 17

Influence of Normality of NaOH on the Critical Ratio

Normality of NaOH.	Critical Ratio.
5 N	0·105
1 N	0·081
$\frac{1}{2}$ N	0·081
$\frac{1}{4}$ N	0·156
$\frac{1}{6}$ N	0·156
$\frac{1}{8}$ N	—[1]

Robertson found that the critical ratio of water to oil remained constant (0·08 for olive oil used) for alkali concentrations above N/200. When the alkali concentration fell below this limit, the amount of oil which could be emulsified in a given volume of water progressively diminished until, when the alkali concentration decreased to N/800, no stable emulsion of oil-in-water was possible. According to Robertson, the important factor throughout is the soap formed by the interaction of the alkali and the free fatty acid in the oil. He argued that while an excess of alkali was maintained, the amount of soap present in the system would be constant. Below a limiting concentration of alkali fixed by the amount of free fatty acid present the soap formed would be insufficient to maintain an emulsion of oil-in-water, a large volume of oil dispersed as globules requiring more than the available amount of soap to form the protecting enveloping film. Such a quantity of soap, however, could envelop *water* in an oil medium, since there would be fewer globules to cover, and consequently the system changes over to the reverse type of emulsion.

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[1] No stable oil-in-water emulsion could be obtained.

Obviously a crucial point in this argument is the assumption that one and the same emulsifying agent can stabilise two emulsions of opposite type. Now the amount of free fatty acid in the oil was unknown in these experiments ; consequently the amount of soap formed is underterminate, as is also its nature. Assuming sodium oleate was formed, why did Robertson obtain two types of emulsion with olive oil and this soap when in the case of benzene and kerosene emulsions sodium oleate only permits the oil-in-water type ? A possible explanation has been given by Bancroft,[1] who believes that sodium oleate is insoluble in kerosene or benzene,[2] whereas in high concentrations of olive oil the solubility of sodium oleate therein may prove a more important factor than the water solubility.

The results obtained might have been different if Robertson had altered his method of emulsification. Instead of shaking all the ingredients together in one operation, the large volume of oil could have been gradually added to the NaOH solution, emulsifying thoroughly after each addition. Undoubtedly more oil could thus have been dispersed in the aqueous phase and the critical ratio considerably diminished. When a large volume of one phase (*e.g.*, oil) and a small volume of the other (*e.g.*, water) are shaken in bulk together, the superior volume of the more abundant phase becomes an important factor.[3] From the purely mechanical aspect of the disintegration of particles, the water-in-oil type of emulsion is promoted.[4]

Robertson's results are of much interest inasmuch as he obtained two sets of emulsions, but they are prejudiced by the fact that the soap concentrations are unknown, and also by the fact that excess of free alkali may exert a particular influence on the system. Seifriz [5] finds that the type of emulsion of light petroleum oils in water, stabilised with casein, is not influenced by alteration of the phase-volume ratio. Heavier petroleum oils, which give unstable oil-in-water-emulsions do, however, give emulsions where the type is a function of the phase-volume.

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[1] *J. Phys. Chem.*, **16**, 746 (1912).

[2] Harkins *et al.*, *J. Am. Chem. Soc.*, **39**, 591 (1917), give the solubility in benzene as 1 in 40,000.

[3] Cf. Sanyal and Joshi, *J. Phys. Chem.*, **26**, 481 (1922).

[4] Cf. Clayton, *Trans. Faraday Soc.*, **16**, Appendix, p. 23 (1921).

[5] *J. Phys. Chem.*, **29**, 838 (1925).

Bhatnagar[1] has also investigated the volume relations in emulsions of olive oil in alkali (KOH), and found that the volume percentage of 74·02 holds when the aqueous phase is very weakly alkaline (N/1,000 to N/500). With alkalies of greater concentration higher ratios were possible,[2] just as obtained by Robertson, but they broke up, yielding a stable cream, possessing the volume ratio 74 : 26. The phase ratios at the critical (inversion) point with different strengths of alkalies were found by Bhatnagar to be :—

KOH c.c.	Olive Oil[3] c.c.	Strength of Alkali.	Volume Ratio at Inversion Point.
25	73·5	0·933 N/1,000	74 : 26
20	58·4	0·933 N/700	75·5 : 25·5
25	72·7	0·933 N/500	74·4 : 25·6
20	75·2	0·933 N/100	79 : 21
10	88·9	0·933 N/50	89 : 11

Bhatnagar believes that the change in a volume ratio with the more concentrated alkali is due to "the solid or gelatinous film" enveloping the oil globules, thus permitting squashing of the globules instead of coalescence on touching.

He next made emulsions containing the majority of the globules as equal spheres. Such were obtained by selecting from a new oil-in-water emulsion, the cream containing approximately 74 per cent. of oil by volume. Small quantities (5 to 10 c.c.) were very vigorously agitated for several hours, until a microscope examination showed the particles to be small and of nearly equal size. Three such homogeneous emulsions were made, using different strengths of KOH, and known amounts were "broken" by a drop of strong HCl. The volumes of the two phases were then measured and checked against the values calculated on the assumption that closest packing has existed in the emulsions, in which case the ratio :

$$\frac{\text{Total volume of emulsion}}{\text{Volume of oil phase}} = 1.35.$$

A very fair agreement was shown.

The results are given in Table 18.

Sanyal and Joshi[4] investigated emulsions of castor oil, olive oil and benzene in sodium oleate solutions. When the ratio : oil phase/water phase exceeded 3 : 1, the emulsions were of the *water-in-oil* type. Evidently the viscosity of the oil is an important factor, as the water-in-benzene emulsions were unstable. When the concentration of the soap solution is 1 per cent. or more, "the nature of the emulsifying agent is

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[1] *J. Chem. Soc.*, **117**, 547 (1920).

[2] Cf. Fischer and Hooker, "Fats and Fatty Degeneration" (1917), p. 41. These investigators obtained stable emulsions up to 95 per cent. of cotton-seed oil in concentrated potassium soap solutions.

[3] Containing 0·5 per cent. free oleic acid.

[4] *J. Phys. Chem.*, **26**, 481 (1922).

TABLE 18

VOLUME RELATIONS IN HOMOGENEOUS EMULSIONS

Emulsion.	Total Volume c.c.	Strength of KOH.	Radii of Uniform Globules.	Volume of Oil Phase.	
				Obs.	Calc.
				c.c.	c.c.
1	7	0·933 N/500	0·0075 mm.	5·09	5·1
2	5	0·933 N/700	0·0070	3·7	3·69
3	5	0·933 N/1,000	0·0055	3·6	3·69

more effective than the volume ratio effect and oil-in-water emulsions only are stable with a soap like sodium oleate." The authors believe "such (water-in-oil) emulsions can well be classified with the mechanical emulsions of Lewis and Ellis because their formation is mechanical." The present writer believes such emulsions are accidental, depending *only* on the method of mixing the solutions.[1]

Certain experiments by Stamm [2] are of interest. Using oleic acid and water, but no emulsifying agent, it was found that emulsions prepared by the acid of a colloid mill were of the oil-in-water type for volume compositions of 5 to 40 per cent. oleic acid, and of the water-in-oil type for volume compositions of 45 to 70 per cent. oleic acid. Similarly, refined petroleum-water mixtures showed a phase-volume effect. With 50 per cent. oil, the emulsion type was water-in-oil, but with 40 per cent. it was the reverse. Phase-volume evidently plays a distinctive *rôle* in a *simple* two-liquid system.

Hatschek [3] has pointed out that the stability of emulsions containing large percentages of dispersed phase is dependent on the phase ratio, and is generally not complete unless the figure corresponding to closest packing is approached. He also mentions the interesting theoretical possibility of an emulsion of two liquids having the same density; such an emulsion should be quite stable, no matter what the value of the phase ratio.

The idea has also been mentioned by Marshall [4] and Woodman.[5] Several patents embody the idea of equalising densities of the two phases to ensure stability. Thus, Imray [6] describes the preparation of stable emulsions of medicaments soluble in oil by using a partially halogenated oil, such that this phase has the same density as the aqueous phase. For example, castor oil is halogenated until about 10 per cent. of its weight of chlorine has been taken up, the density rising to 1·02. The oil may now be emulsified with a gum solution of the same density.

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[1] See p. 342.

[2] *J. Phys. Chem.*, **30**, 998 (1926).

[3] *Brit. Assocn. Colloid Reports*, **2**, 17 (1918).

[4] *Pharm. J.*, **28**, 264 (1909).

[5] *J. Pomol. Hort. Sci.*, **4**, 193 (1925).

[6] Brit. 200,036 (1923). Cf. Lafarge and Chanut, Fr. 751,045 (1933).

Similarly, Hartman and Kägi[1] emulsify a solution of camphor in brominated olive oil with an aqueous solution of sodium caseinate. Mecke[2] suggests for paints and colour emulsions an organic chloride be dissolved in drying oils and the solution mixed with dilute ammonia. The density of the oil thus approaches that of water, the other liquid in the subsequent emulsion.[3]

Trux[4] utilises the same idea in dispersing bitumen in aqueous solution of sodium silicate of density equal to that of the bitumen.

Valuable as is this notion of equalising the densities of the two phases, it must be realised that density is subsidiary to the influence of interfacial tension and viscosity. Sata and Haruhiko[5] have well illustrated this. Their data may be summarised as follows :—

Phase-volume maximum ratio.	1st Phase.	2nd Phase.	I.T. dynes/cm.
3 : 2	Water	$C_6H_6 + CCl_4$	36·6
2·5 : 2·5	Water	Iso-amyl alcohol + $CHCl_3$	11·4
1·5 : 3·5	Water + methyl alcohol	C_6H_6	3·6

Emulsions were readily prepared by shaking, but on standing they soon broke.

OPTICAL PROPERTIES OF EMULSIONS

Singularly few publications concern the optical properties of emulsions. Several papers by Krishnan[6] deal with the reciprocity theorem in colloid optics and include data on emulsions. The nephelometer has been used to determine the fat content of emulsions by Mészáros,[7] Bloor,[8] Ellis,[9] and Woodman, Gookin and Heath.[10] Katsurai[11] has investigated the Tyndall effect in milk.

However, these are quite incidental incursions into the optics of emulsion systems. The subject is beset with difficulties and much remains to be investigated. The most important contribution so far is that by Bailey, Nichols and Kraemer,[12] dealing with particle size and optical properties. They point out that many attempts have been made to calculate theoretically the dependence of the light-scattering power of suspensions upon the size and refractive index of the particles, the refractive index of the medium, and the wave-length of light used. Rayleigh's treatment [1] for infinitely small, non-absorbing particles in a non-absorbing medium becomes only approximate when the particle size approaches the order of magnitude of the wave-length of light, or if the particle is coloured.

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[1] U.S. 1,611,190 (1926). Cf. Volck, U.S. 1,914,902 (1933).

[2] Ger. 368,234 (1922).

[3] Cf. Fleming, *Ind. Eng. Chem.*, **17**, 1087 (1925). See also Marshall, *J. Gen. Physiol.*, **13**, 637 (1930).

[4] Ger. 505,106 (1927). See also Dunlop, Brit. 422,568 (1933).

[5] *Bull. Chem. Soc., Japan*, **14**, 135 (1939).

[6] *Proc. Indian Acad. Sci.*, **1A**, 717 ; 782 (1935) ; **7A**, 21 (1938) ; **10A**, 395 (1939) ; *Current Sci.*, **6**, 90 (1937). See also Subbaramaiya, *Proc. Indian Acad. Sci.*, **1A**, 709 (1935) ; Gans, *Physik. Z.*, **38**, 625 (1937) ; Procopiu, *Compt. rend.*, **201**, 55 (1935) ; Rao and Muthuswami, *J. Annamalai Univ.*, **6**, 107 (1937).

[7] *Z. Unters. Lebensm.*, **69**, 321 (1935).

[8] *J. Biol. Chem.*, **17**, 377 (1914) ; *J. Am. Chem. Soc.*, **36**, 1300 (1914).

[9] *Z. physik. Chem.*, **80**, 597 (1912).

[10] *Ind. Eng. Chem.*, **8**, 128 (1916) ; cf. Baldwin, *ibid.*, **19**, 78 (1927).

[11] *Kolloid Z.*, **67**, 143 (1934) ; **74**, 287 (1936).

[12] *J. Phys. Chem.*, **40**, 1149 (1936).

It is essential to work with suspensions of absolutely uniform particle size and the authors employed the Svedberg ultracentrifuge for this purpose. However, this apparatus does not give directly a particle-size distribution and somewhat involved calculations are necessary to relate light scattering to particle size. "Specifically, a particle-size distribution may be expressed as a relationship between dc/dr and r, where dc/dr is proportional to the weight of particles having a radius between r and $r + dr$. The ultracentrifuge, however, gives the relation between $d(kc)/dr$ and r, where k is the apparent absorption coefficient of a suspension of particles of radius r. For a suspension of colourless particles in a colourless medium, the 'absorption' is, of course, entirely due to scattering, and the 'absorption coefficient' in such cases provides a measure of the light-scattering power of the suspension. The relation between $d(kc)/dr$ and r we call a *weight-optical distribution,* and since k in general varies with r, the weight-optical distribution normally is not identical with the true weight-distribution curve."

A mechanical product-integraph was used to determine the relation between absorption coefficient (as a measure of light scattering) and radius of particles in a medium of specified refractive index, analysing the weight-optical distribution curves for systems with different particle sizes.

A stock emulsion of Nujol in 76 per cent. glycerol containing 1 per cent. of Castille soap was homogenised and from it a series of emulsions of identical grain-size distribution was prepared, the light-scattering properties being greatly varied by reducing the refractive index of the medium by dilution with aqueous glycerol mixtures. Six emulsions with the dispersion medium varying from 15 to 76 per cent. glycerol were so prepared, corresponding to a range of refractive index of the medium from 1·359 to 1·144 at a wave-length of 444 millimicroms, where the absorptions and weight-optical distributions were measured. At the same wave-length, the refractive index of the Nujol is 1·488.

The authors' paper gives the graphical representation of the data obtained, but the relation of the experimental results to theoretical calculations of light scattering is reserved for some future publication.

COLOUR AND OPACITY OF EMULSIONS

The mixing of an aqueous liquid with an oil usually results in a creamy emulsion due to the differing refractive indices and optical dispersive powers of the two phases. Morse [2] has studied the opacity of emulsions as influenced by the concentration and degree of dispersion of the internal phase and the subsequent effect on the final colour of the emulsion should one of the phases be coloured.

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[1] *Phil. Mag.*, **47**, 375 (1899).

[2] *Trans. Faraday Soc.*, **33**, 941 (1936). See Amy, *Compt. rend.*, **207**, 329 (1938

Toussaint's method[1] of recording reflection or transmission by a galvanometer connected to a photo-electric cell on which the light falls after leaving the experimental sample was employed, six Wratten filters permitting predominant wave-lengths throughout the visible spectrum.

It was observed that irrespective of (1) the particular colour employed (2) in which phase it is present, and (3) the type of emulsion (O/W or W/O), the final colour effect depends on the opacity of the emulsion. This in turn depends on the refractive indices and optical dispersive powers of the two phases and on the concentration and globule size of the internal phase.

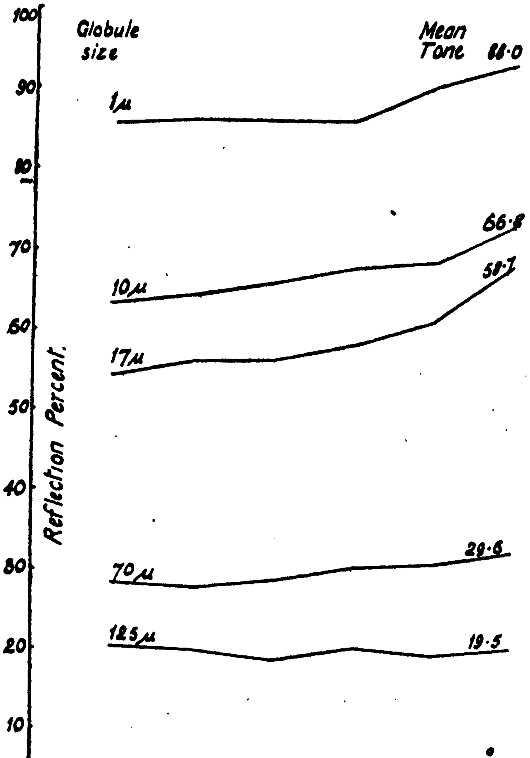

FIG. 21.

With the refractive indices and optical dispersive powers maintained constant, the effect of the concentration and the globule size of the internal phase was examined. Emulsions of liquid paraffin were used as a colourless oil is essential. An aqueous solution of gums was the external phase. Various methods were adopted to prepare emulsions of different grain-size, with oil concentrations of 5, 10, 15, 20 and 50 per cent.

Fig. 21 gives the "colour" curves of 10 per cent. emulsions of varying grain sizes. The average of the six values gives the mean tone and in Fig. 22, these mean tones are plotted as percentage "opacities" against globule size for a range of oil concentrations. During the recording of a large number of these "opacities," it was found that the "mean tone" closely corresponded to the percentage reflection using the yellow filter, wave-length 5400Å, and in subsequent work this figure was taken as the opacity.

It will be seen from Fig. 22 that a layer of emulsion 1 cm. deep will appear equally opaque and white irrespective of the fact that the dispersed phase may be 5 per cent. or 50 per cent., provided that the globule size is in the neighbourhood of 1 μ.

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[1] See L. Blin Desbleds "Exact Colour Matching and Specifying" (Paris).

Maintaining a uniform globule size the effect of concentration was investigated. Emulsions of 25 per cent. liquid paraffin were prepared. When a 25 per cent. emulsion of sufficiently uniform globule size had been obtained, it was diluted to give a series of concentrations, the opacity of each one being recorded. Fig. 23 shows such a series at various globule sizes. Some discrepancy in opacity at the larger globule sizes is evident between this series and those in Fig. 22, no doubt due to the less uniform emulsions of the latter. At dilute concentrations the effect of globule size is most marked and any irregularities have a pronounced effect.

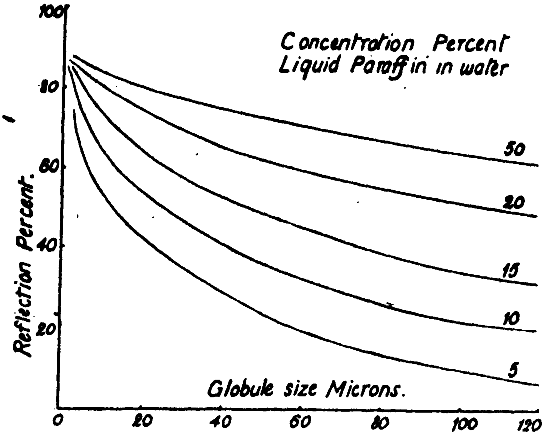

FIG. 22.

Figs. 22 and 23 give a guide to the relative opacities to be expected with emulsions in which the phases have optical properties corresponding to those of liquid paraffin and aqueous gum solution. If a coloured solute be present in one of the phases of the emulsion, the resulting colour of the emulsion is a function of the opacity.

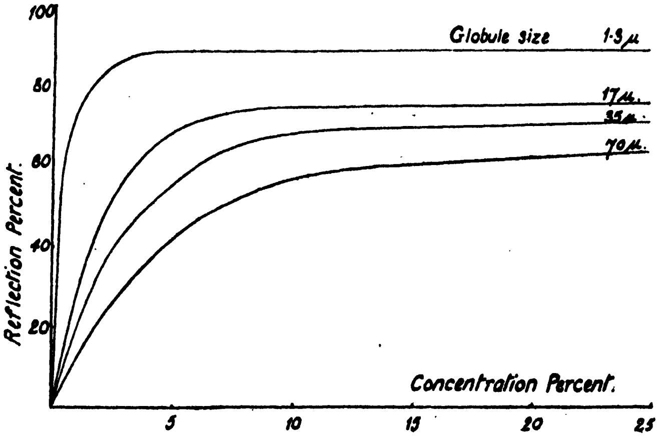

FIG. 23.

TRANSPARENT EMULSIONS

Emulsions of the oil-in-water type are usually white or pale yellow in colour. Very dilute emulsions, such as those prepared by Lewis, are practically clear in transmitted light, but show a bluish tinge in reflected light. The more concentrated the oil phase, the more pronounced becomes the white or creamy colour. Some emulsions are coloured owing to the presence of a colouring substance in the oil, *e.g.*, butter, which contains carotin and xanthophyll pigments. Margarine is coloured artificially, certain oil-soluble azo-dyes being used for this purpose.

Transparent emulsions are possible when the two liquids have the same values for the refractive index and optical dispersive power. Thus glycerol gives transparent emulsions in a solution of calcium oleate in carbon tetrachloride. Transparent emulsions of glycerol are also possible in liquid paraffin containing 2 per cent. of crêpe rubber as the emulsifying agent.

The production of transparent emulsions has been made the subject of a patent by Rector,[1] who proposes to make medicinal emulsions (*e.g.*, of cod liver oil) transparent by bringing the refractive indices of the phases into closer similarity through the addition of salt or sugar. Fleming [2] describes the preparation of a transaprent emulsion of carbon disulphide for use as an insecticide.

An interesting application has been described by Whitmore and Linehan,[3] who prepared transparent emulsions of several essential oils as food flavours. Some of the essential oils possess high refractive indices, but these were reduced by adding the mutually soluble ethyl esters of coconut oil. The aqueous phase contained 80 per cent. of total sugars (2 parts invert sugar and 1 part sucrose), gelatin or gum arabic being present as emulsifying agent. Such emulsions contained 5 per cent. by volume of essential oil and, to instance the orange oil emulsion, the refractive index at 25° C. of each phase was 1·4690. Whilst the transparency of the systems was only slightly affected within the temperature range 20° C. to 30° C., outside this range the emulsions became opaque.

CHROMATIC EMULSIONS

Emulsions with structural colours—so-called " chromatic emulsions " —have been prepared by Bodroux [4] and by Holmes and Cameron.[5] These investigators showed that if emulsions be made of two liquids of equal refractive indices (ensuring transparency), but widely different optical dispersive powers (n_F—n_C), the system is comparable to a multitude of lenses or prisms, with consequent prismatic colour effects.[6]

The continuous phase of the emulsion must contain two completely miscible liquids, one of them of high refractive index and high optical dispersive power. Gradually adding this mixture to a milky emulsion already at hand makes it possible to change gradually the refractive index and optical dispersive power of the emulsion, thus producing the chromatic range of colours. Holmes and Cameron prepared several emulsions exhibiting such colour effects, *e.g.*, potassium iodide in water has a high optical dispersive power and high refractive index; if a solution of K I be added to an emulsion of "Nujol" in sodium oleate solution, prismatic colours are secured. Change in temperature causes change in colours, owing to the unequal temperature effect on the optical dispersive powers of the phases.

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[1] U.S. 1,389,161 (1921); *vide* also *Chem. Age* (N.Y.), **29**, 408 (1921). A similar patent has been granted to Whatmough, U.S. 1,663,323 (1928).

[2] *J. Agr. Research*, **33**, 17 (1926).

[3] *Ind. Eng. Chem.*, **21**, 878 (1929).

[4] *Compt. rend.*, **156**, 772 (1913). See also Ostwald, " Licht und Farbe in Kolloiden " (Dresden, 1924), p. 16.

[5] *J. Am. Chem. Soc.*, **44**, 71 (1922).

[6] This is really a special case of the Christiansen effect [*Wied. Ann.*, **23**, 298 (1884)] a good *résumé* of which is given by Wood: " Physical Optics " (New York: 1934), p. 115. See also Lord Rayleigh, *Phil. Mag.*, **20**, 358 (1885).

These results were confirmed and extended by Bhalla, Bhatnagar and Yajnik.[1] Thus, dispersing 92 c.c. of glycerol in 14 c.c. of acetone by the aid of collodion, they obtained a milk-white emulsion. To a constant volume of this emulsion (12 c.c.), carbon disulphide was added by drops, followed by shaking. Various colours were then secured:—

45 drops CS_2 ⟶	yellow (transmitted),	blue (reflected).
46 ,,	brown ,,	blue ,,
47 ,,	red ,,	green ,,
48 ,,	blue ,,	green ,,
49 ,,	blue.	
50 ,,	bluish-white.	
51 ,,	milky.	

Addition of acetone or amyl acetate by drops to the last-mentioned milky emulsion produced the above colour sequence in reverse order.

The authors distinguish between two types of chromatic emulsions, (A) the colour changes through blue → lavender → brown → yellow, as the temperature is raised, and (B) the colour changes in the reverse order under the same condition. This phenomen is apparently connected with the relative volatilities of the two constituents of the external phase. Type A is illustrated by a glycerol-in-acetone emulsion to which is added CS_2, whilst glycerol-in-acetone emulsions containing benzene, toluene or benzyl acetate illustrate Type B.

A comprehensive investigation on the optical properties of chromatic emulsions has been carried out by Sogani,[2] following on the qualitiative studies by Sethi working with glycerol/turpentine emulsions. Sogani[3] employed emulsions as described by Holmes and Cameron, and he studied:—

(*a*) The spectral range of the light transmitted by the emulsions.

(*b*) Their refractivity and the character of the diffraction haloes produced by them.

(*c*) The surface colours of the emulsions.

(*d*) The influence on optical properties of the factors: dispersive powers of the liquids used, globule size, and the depth of the emulsion examined.

"Probably the most interesting new phenomenon noticed is that the light scattered by an emulsion in which the disperse phase consists of droplets of uniform size closely packed together is concentrated in sharply defined circular diffraction rings, the effect being somewhat analogous to that obtained with monochromatic X-rays in the powder method of crystal analysis."

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[1] *Kolloid-Z.*, **43**, 366 (1927).

[2] *Phil. Mag.*, **1**, 321 (1926). Detailed theoretical treatment has been published by Knudsen, *Kolloid-Z.*, **66**, 257 (1934).

[3] *Proc. Ind. Assocn. Cult. Sci.*, **6**, 134 (1920–1921).

It was found that transparent emulsions transmit the complete spectrum. With emulsions of *non-uniform* globule size, the region of transmission depends on several factors. Thus, it widens as the intensity of incident light increases and as the globule size is decreased. Increasing the concentration of the disperse phase narrows the region of the spectrum transmitted, approaching a limit in the case of close packing. Practically the complete spectrum is transmitted through a layer of emulsion of the order of 0·1 mm. thick, but the region decreases as the emulsion depth is increased. The greater the difference between the dispersive powers of the phases, the narrower is the spectrum region transmitted.

Still confining attention to non-uniform emulsions, interesting details are given relating to the light-scattering by a close-packed emulsion. Illumination with a point source of white light gives a continuous halo of fine mottled structure wherein the colour changes from place to place. This halo appears to surround the point source which naturally shows the colour of the transmitted light, whilst the succession of colours in the halo depends on the region of transmission. Using monochromatic light produces a halo the size of which is a minimum for that wave-length where the two phases of the emulsion possess the same refractive index. Increase in size of the halo occurs with increase in intensity of the incident beam, the thickness of the emulsion and the concentration of the internal phase. As the diameter of the globules increases the size of the halo decreases.

When a wave of light is incident to an emulsion, its path will lie partly through the internal phase and partly through the external phase. "The emulsion as a whole will therefore have a definite refractive index and disperse power of its own as distinct from those of either phase and of course intermediate between them." The refractive index μ_e of close-packed emulsion will be

$$\mu_e = \frac{2\mu}{3} + \frac{\mu'}{3}.$$

with μ and μ' are the refractive indices of the internal and external phases respectively. Similarly, the dispersive power of the emulsion will be

$$d_e = \frac{2d}{3} + \frac{d'}{3}.$$

In the case of a close-packed emulsion containing *uniform* globules, the ordinary continuous halo is replaced by "a beautiful system of maxima and minima, the rings increasing remarkably in size as the surface of separation is approached. The region surrounding the source is dark, then follows a fairly sharp bright ring bluish on the inside and reddish on the outside." A monochromator is recommended for proper study of this phenomenon. The scattered light completely disappears when the wave-length is such that $\mu = \mu'$.

Owing to the uniform size of the globules, interference is possible between the waves scattered by them, and maxima and minima arise. Since the light scattered by any particular row of globules in a given layer necessarily passes through the entire layer, all the colours are not equally represented in the ring. Those wave-lengths approximating the point $\mu = \mu'$ alone have a chance of getting through.

Finally, Sogani observed that sparkling colours are exhibited on both sides of the surface of separation of the emulsion and free external phase. Observation may be made from both sides of the boundary surface at nearly glazing incidence. An emulsion of glycerol in acetone + benzene was employed to facilitate a spectroscopic study of the light reflected from the two surfaces. The colours were found to be due to total reflexion, the emission as a whole having a dispersive power different from that of the clear liquor.

The experimental technique for the optimum preparation of chromatic emulsions of cod-liver oil has been described by Narwani.[1]

THE VISCOSITY OF EMULSIONS

The viscosity of a liquid is its internal friction, *i.e.*, its resistance to shear, agitation or flow. Viscosity is measurable in absolute units, viz., the *poise*, which is defined [2] as the force required to produce a difference in the velocity of flow of a liquid of 1 cm. per second, when this force is exerted on 1 cm.^{2} between two parallel planes, each 1 cm.^{2} in area and 1 cm. apart. The reciprocal of absolute viscosity is the fluidity. Viscosities are frequently expressed in *centipoises*, *i.e.*, in $\frac{\text{poise}}{100}$, and the standard for usual reference is the viscosity of water at 20° C., viz., 1·0050 centipoise.

There is a distinction between viscosity and plasticity ; in the former, the ratio : $\frac{\text{shearing stress}}{\text{rate of shear}}$ is a constant, whilst plasticity is known by the fact that this ratio varies with the rate of shear.[3] A plastic system requires the expenditure of energy to cause it to " yield " before plastic flow begins, and hydrophile colloids such as gelatin hydrosols are of this type and are characterised by viscosity values much greater than that of the pure solvent.

Various methods are employed for the measurement of viscosity, but their relative merits and the theoretical foundations of their use are beyond the scope of this volume.[4] The various methods though giving comparable results for pure liquids and true solutions yield discordant data in the case of colloid systems due to the plastic nature of the colloids set up by a definite structure in solution, such "structural viscosity" being particularly evident with a sol capable of undergoing gelation.[1] The sulphonated oils furnish special examples of systems which in aqueous "solution" exhibit structural viscosity, depending on the concentration of the "solution" and the *p*H value, as well as on the particular sulphonated oil under investigation.[2]

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[1] *Kolloid Z.*, **70**, 297 (1935).

[2] Deely and Parr, *Phil. Mag.*, **26**, 87 (1913) ; Barr, *World Petroleum Cong.* (London, 1933).

[3] See Herschel, Alexander's " Colloid Chemistry " (New York, 1926), Vol. I., p. 727 ; Hatschek, *ibid*, p. 738 ; Ostwald, " Handbook of Colloid Chemistry " (London, 1919), p. 145 ; Bingham, " Fluidity and Plasticity " (New York, 1922), and in Alexander's " Colloid Chemistry," Vol. I., p. 720 ; also in *World Petroleum Cong.* (London, 1933) ; Hanstock, *J. Soc. Chem. Ind.*, **57**, 1214 (1938) ; Mack, *ibid.*, **58**, 306 T (1939) ; Blott and Samuel, *Ind. Eng. Chem.*, **32**, 68 (1940) ; Houwink, " Elasticity, Plasticity and Structure of Matter " (Cambridge, 1937) ; Richardson, *Physics*, **6**, 273 (1935) ; Second Report on Viscosity and Plasticity, *Committee for the Study of Viscosity of the Academy of Sciences in Amsterdam.* (In English, 1938, pp. 276.)

[4] Hatschek's " Viscosity of Liquids " (London, 1928) gives full details.

The position regarding the viscosity of emulsions from a *quantitative* point of view is far from satisfactory, limited research being done in this connection. *Dilute two-phase emulsions* show a viscosity not greatly exceeding that of water. Viscosity increases rapidly in other emulsions as the volume of the dispersed phase increases,[3] but in this case, of course, there arises the new factor of the presence of the emulsifying agent. The viscosity of concentrated emulsions is intimately connected with the presence of adsorbed films at the dineric interface. The homogenisation of such emulsions confers a marked increase in the viscosity of the system, as the increased dispersion of the internal phase greatly extends the contacting boundary between the two phases and provides for greatly increased adsorption of the emulsifying agent.[4]

Hatschek,[5] assuming that the dispersed phase of an emulsion occupies at least 50 per cent. of the total volume, has deduced a formula for the viscosity of an emulsion, viz :—

$$\eta' = \eta_e \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1}$$

where η' = coefficient of viscosity of the emulsion,
η_e = ,, ,, ,, ,, external phase,
$A = \text{ratio}, \dfrac{\text{Total volume of emulsion}}{\text{Volume of dispersed phase}}$.

If $\eta_e = 1$, the expression may be transformed thus :—

$$A = \left(\frac{\eta'}{\eta' - 1}\right)^3.$$

Beck[6] found that emulsions of castor oil in water up to 10 per cent. of oil possessed viscosities little different from that of water. With 4 per cent. of gum arabic as the emulsifying agent the viscosities of the emulsions showed a marked increase as the oil content was increased to 20 per cent.

Recently, Kremann, Griengl and Schreiner[7] have determined the viscosities of the emulsions obtained by strongly agitating at 50° . " the purest olive oil " with water and aqueous solutions of NaOH and HCl. The values obtained varied as the relative amounts of oil and aqueous phase. Their data with oil and water only are given as a graph in Fig. 24.

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[1] Hatschek, *Kolloid-Z.*, **13**, 88 (1913) ; Hess, *ibid.*, **27**, 154 (1920) ; Rothlin, *Biochem. Z.*, **98**, 34 (1919) ; Ostwald, *Kolloid-Z.*, **43**, 190 (1927).

[2] Schindler and Flaschner, *Kolloid-Z.*, **48**, 328 (1929).

[3] Cf. Varadhan and Watson, *J. Indian Inst. Sci.*, **13A**, 21 (1930) ; Parke, *J. Chem. Soc.*, **1934**, 1112.

[4] See p. 391.

[5] *Kolloid-Z.*, **7**, 301 (1910) ; **8**, 34 (1911) ; **11**, 284 (1912) ; **12**, 238 (1913) ; *Trans. Faraday Soc.*, **9**, 80 (1913). See also Smoluchowski, *Kolloid-Z.*, **18**, 190 (1916).

[6] *Z. physik. Chem.*, **58**, 409 (1907).

[7] *Kolloid-Z.*, **62**, 61 (1933).

It is evident that up to about 23 per cent. of oil, the viscosity of the emulsion obtained is relatively little greater than that of water; thereafter, increase in the oil content produces a very rapid increase in viscosity, a maximum being obtained at 25 per cent. of oil. Further increase in the amount of oil leads to a fall in the viscosity of the resulting emulsion. The results are connected with the *type* of emulsion and illustrate the influence of phase-volume ratio in emulsion (see p. 342). It was noted that the W/O emulsions were very unstable.

Fig. 25 illustrates the relation between the maximum value of η and

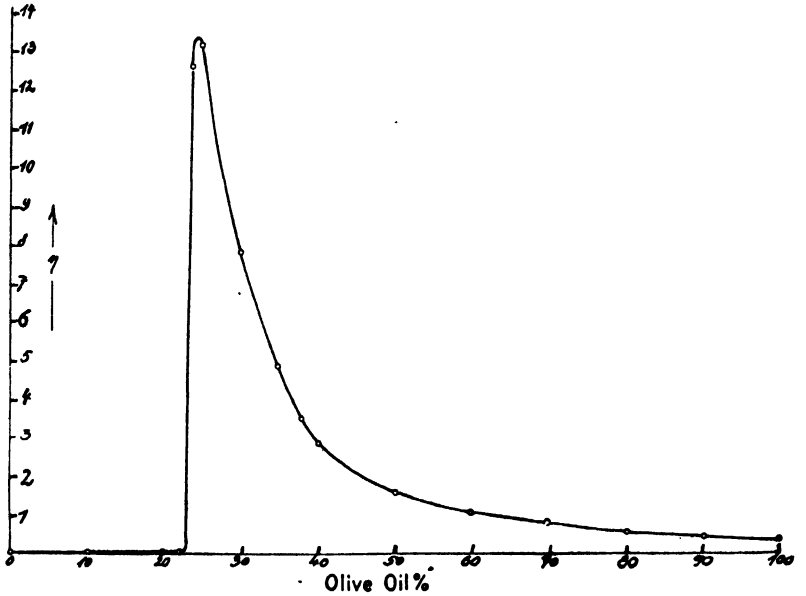

FIG. 24. The viscosity of O/W emulsions as a function of the percentage of oil dispersed.

the normality of the NaOH and HCl solutions agitated with varying amounts of the oil. (Presumably, the maximum in the curve on the NaOH side will depend on the free fatty acid content of the oil.) Another set of graphs given by the authors is highly interesting, showing that dependence of the oil content of the emulsion and the pH value, when η is a maximum. As the concentration of NaOH increases, the maximum value of η is attained at higher oil quantities and with O.IN.NaOH, η is a maximum when the oil is 75 per cent., *i.e.*, at closest packing of the oil globules.

Bearing on these results are the experiments of Kremann, Griengl and Schreiner [1] on the viscosity of powerfully-stirred mixtures of liquids of limited miscibility, notably phenol and water, which exhibit maximum viscosity and can be regarded as model systems which are transitititional to the emulsion colloids. By suitable addition of acid and alkali, marked peptisation occurs hand in hand with decreasing viscosity, corresponding to increasing dispersion in the direction of molecularly dispersed systems. The value and sign of the electric charge on the interfacial layer play a special *rôle* in this viscosity effect, through their influence on the degree of dispersion.

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[1] *Sitz. Akad. Wiss. Wien.*, Abt. IIb., 141, 790 (1932).

An extension of these experiments was made by Pestemer and Birkmann.[1] Comparison of the viscosity curves for the systems : olive oil/water, phenol/water and benzene/water, shows that the last-mentioned possesses the least marked maximum. This is probably due to less stable and less dispersed condition of the mixture, and a smaller electric charge at the interface. This charge depends on the dipole moment of the benzene, which is much less than that of phenol or olive oil. Paraffin oil has a dipole moment almost zero, and as examination of the viscosity curve for the system paraffin oil/water shows, there is no maximum viscosity, but two changes of direction in the curve. The first is in the field of the water-rich mixture, up to 57 per cent. of paraffin oil, which exhibits viscosity but little greater than that of water, corresponding to oil-in-water emulsions. The second branch of the curve occurs when the mixture corresponds to about 10 per cent. of water and 90 per cent. of oil, corresponding to an emulsion of water-in-oil. These changes of direction in the viscosity curve are pronounced when the paraffin oil is replaced by a vaseline oil, a typical S-form of curve being the result. With these mineral oils the effect of acid or alkali in conferring an electric charge to the interface is trivial.

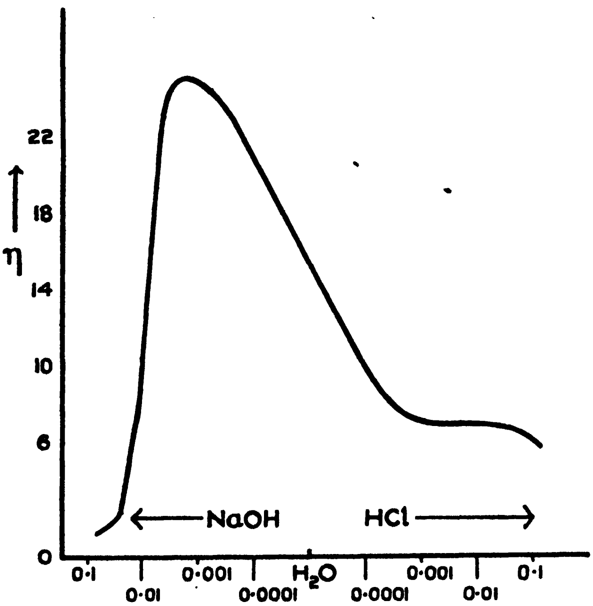

FIG. 25. Variation in the maximum viscosity of O/W emulsions with acidity and alkalinity.

The above investigations suffer from the fact that although a stirrer operating at 800 r.p.m. is mentioned as being employed to effect dispersion, no analysis is made of the uniformity or otherwise of the dispersion, and the grain-size of the emulsions is not stated.

Discussions on the viscosity of colloid systems usually commence with the investigations by Einstein[1] on the viscosity of a fluid containing in suspension small solid spheres. Assuming rigid spheres possessing diameters small in relation to the distance between their centres, although large in relation to molecular dimensions, Einstein obtained the equation :

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[1] *Kolloid-Z.*, **65**, 25 (1933).

$$\eta' = \eta(1 + 2{\cdot}5\phi)$$

where η' = mean viscosity of the suspension,
η = viscosity of the liquid medium,

$$\phi = \text{ratio} : \frac{\text{volume of spheres}}{\text{total volume of suspension}}$$

It should be noted that no term is included for the size of the spheres.

The extension of Einstein's treatment to emulsions presents difficulties, since the correct boundary conditions are not known and globules of liquid may be deformed due to the combined action of viscous forces and interfacial tension. In the case of two-phase emulsion, preliminary investigations by Richardson[2] seem to show that the viscosity of each liquid in the proximity of their interface is uninfluenced by the interfacial tension. More extended observations are required, however, with water and a series of organic liquids with different orientation possibilities. In passing, attention may be directed to the work of Smith[3] on 'interfacial viscosity' as influenced by the presence of powders in the dineric interface.

Taylor[4] has studied the problem of the viscosity of emulsions. To extend Einstein's analysis, Taylor assumes : (*a*) the globule radius is so small that the spherical condition is maintained, (*b*) slipping at the surface of the globule is *nil*, (*c*) " the tangential stress parallel to the surface is continuous at the surface of the drop, so that any film which may exist between the two liquids merely transmits tangential stress from one fluid to the other." For emulsions, Taylor deduces the equation:

$$\eta' = \eta_e \left\{ 1 + 2{\cdot}5\phi \left(\frac{\eta_i + \frac{2}{5}\eta_e}{\eta_i + \eta_e} \right) \right\}.$$

where η' = viscosity of the emulsion,
η_i = „ „ „ internal phase,
η_e = „ „ „ external phase,

$$\phi = \text{ratio} : \frac{\text{volume of globules}}{\text{total volume of emulsion}}.$$

Meagre work has been published on the viscosity of those emulsions of interest to technical chemists, with the exception of studies on milk and cream, which are really very complicated systems. Investigation is complicated by the fact that the oil hydrosols are so dilute, whilst three-phase emulsions must take account of such factors as the nature of the third phase, the degree of dispersion, the phase-volume ratio, the possibility of occluded air and, finally, the type of emulsion.

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[1] *Ann. Physik.*, **19**, 289 (1906); **34**, 591 (1911); *Kolloid-Z.*, **27**, 137 (1920); Eirich, Bunzl and Margaretha, *ibid.*, **74**, 276 (1936); Boutaric, *Compt. rend.*, **207**, 802 (1938); Staudinger and Husemann, *Ber.*, **68B.**, 1691 (1935); Mardles, *Nature*, **145**, 970 (1940).

[2] *Kolloid-Z.*, **65**, 32 (1933).

[3] *Phil. Mag.*, **4**, 820 (1927).

[4] *Proc. Roy. Soc.*, **A 138**, 41 (1932).

An investigation by Leviton and Leighton[1] concerned the viscosity of emulsions where milk fat was dispersed in skim milk, concentrated skim milk, diluted skim milk and a very viscous solution of sucrose in skim milk. It was sought empirically to determine the relationship obtaining between the viscosity of an emulsion and (*a*) the concentration of the internal phase, (*b*) the composition of the external phase, and (*c*) the degree of dispersion of the internal phase.

The viscosity data conformed to those deduced from the authors' equation :

$$ln\frac{\eta'}{\eta_e} = 2{\cdot}5\left(\frac{\eta_i + \frac{2}{5}\eta_e}{\eta_i + \eta_e}\right)(\phi + \phi^{\frac{5}{3}} + \phi^{\frac{11}{3}})$$

For small values of ϕ of the equation reduces to that of Taylor. Quoting the authors : " The form of the equation and the constant occurring in it are independent of the milk-solids-not-fat content of the continuous medium. The equation may be reduced for dilute emulsions to that derived by Taylor, regardless of the composition or the viscosity of the continuous medium. Consequently, the designation of the suspension, containing particles small in size relative to the fat globules, as the continuous medium is justified, and the validity of the application of Taylor's equation to the emulsions under investigation may be considered to be established. The multiplication of the constant 2·5 in the Einstein equation by the term

$$\frac{\eta_i + \frac{2}{5}\eta_e}{\eta_i + \eta_e}$$

to compensate for the currents set up within the particle, when the dispersed phase is fluid, is supported by the experimental results. Thus, η_i may be varied by the addition of water, condensed skim milk, or cane sugar to skim milk, so that the expression $\frac{\eta_i + \frac{2}{5}\eta_c}{\eta_i + \eta_e}$ is varied from 2·27 to 2·45, and yet the calculated values of the ratio between the viscosity of the emulsion and that of the continuous medium agree within experimental error with the measured values."

A number of papers illustrate the complexities of viscosity data and their interpretation for emulsions. Richardson[2] prepared emulsions of benzene and water, using Na oleate for the O/W type and Mg oleate for the W/O type, both soaps being in 5 per cent. solution. Prepared by intermittent shaking, the emulsions were then homogenised by Briggs' method. Unfortunately, no data were recorded as to the degree of dispersion attained. Viscosities were measured with the Couette apparatus, which consists of two concentric cylinders, the outer rotatable at will. The emulsion is contained in the space between the cylinders and any communicated rotation of the inner cylinder may be measured by its angular deflection from normal. The results obtained were graphically represented by plotting as abscissæ the velocity of the outer cylinder and as ordinates the deflection of the inner cylinder. Fig. 26 is reproduced from Richardson's paper, and gives the graphs of the function : angular velocity deflection for benzene-in-water emulsions of different concentrations of benzene.

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[1] *J. Phys. Chem.*, **40**, 71 (1936).

[2] *Kolloid-Z.*, **65**, 32 (1933).

The curves depart more from the straight line graph (which is typical of a constant viscosity coefficient) the greater the amount of the internal phase. Also, the viscosity decreases as the shearing velocity increases. If, however, a mean velocity of rotation of the outer cylinder be chosen, the graph showing the relation between viscosity and emulsion concentration as in Fig. 27 which includes the type W/O emulsion.

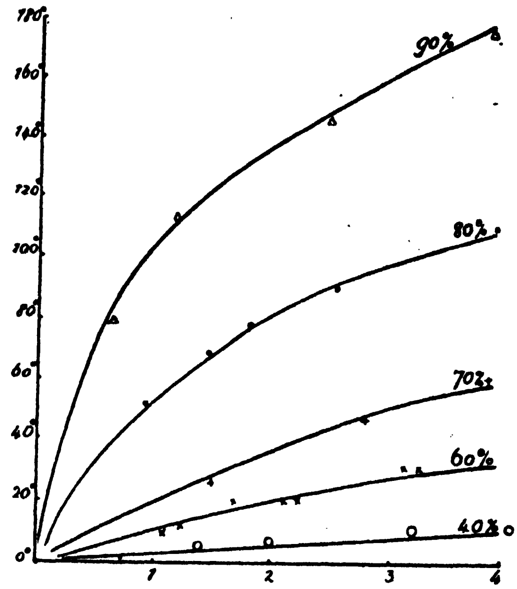

FIG. 26. Curves of the function : angular velocity deflection for O/W emulsions.

With increasing concentration of the internal phase the viscosity of the emulsion increases, so that in the region appraoching 100 per cent. the consistency of margarine is reached.

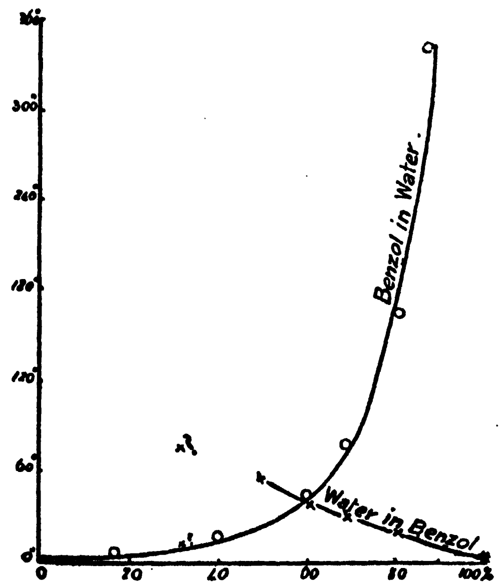

FIG. 27. Relation between viscosity and emulsion concentration.

Richardson has developed an equation from theoretical principles for the viscosity-concentration function, whereby for an arbitrarily chosen mean velocity :

$$\eta' = \eta_e e^{k\phi}$$

$$\text{or, } \log \frac{\eta'}{\eta_e} = k\phi.$$

Plotting the log equation with concentration (ϕ) as abscissæ, and $\log \frac{\eta'}{\eta_e}$ as ordinates, gives a straight line, the slope of which gives the average value of k. For the author's results, $k = 6$, whilst applying the equation to the data of Joshi[1] for oil-in-water emulsions he obtains $k \doteqdot 5$.

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[1] *Trans. Faraday Soc.*, **20**, 512 (1925).

Important work on the viscosity of emulsions has been reported by Sibree,[1] working under Hatschek. Primarily, the investigation was undertaken to test Hatschek's conclusions that there is a variation in the viscosity of an emulsion as the velocity gradient varies, the viscosity becoming constant above a certain velocity gradient. In the constant region, Hatschek's equation for the viscosity of an emulsion is :

$$\eta' = \eta_e \frac{1}{1 - \sqrt[3]{\phi}},$$

and this equation neglects the viscosity of the internal phase. Sibree investigated this point and also the effect of ageing of the emulsions on their viscosities.

The phases employed were 1 per cent. Na oleate aqueous solution and paraffin + bromoform, both phases possessing the same density. Emulsification was effected at 21·5° C. by two methods : (1) Briggs' intermittent agitation [2] and (2) Hatscheks' inspiration method.[3] The primary emulsions contained 50 per cent. internal phase (the organic liquids). Viscosities were determined by means of the Hatschek modification of the Couette apparatus, the deflections being read by means of a telescope and scale.

It was first ascertained that the viscosity of the soap solution is not related to the velocity gradient, and that " the variation in viscosity observed in the emulsions is a function of their structure, and none of it is caused by anomalies of the soap solution."

To illustrate Sibree's data, Table 19 is modified from his publication and deals with a 50 per cent. emulsion of viscous paraffin weighted with bromoform in 1 per cent. aqueous Na oleate solution at 21·5° C., the emulsion being twenty-four hours old.

If the experimental results are plotted with angular velocity (degrees/sec.) as abscissæ and the actual scale deflections (in millimetres) as ordinates, it is obvious that the moment increases less rapidly than the angular velocity of the outer cylinder, *i.e.*, the emulsion does not exhibit a constant viscosity coefficient, this decreasing with increase in the angular velocity of the outer cylinder. Again, the data may be plotted with the angular velocities as abscissæ and the viscosities as ordinates. Below of the region of turbulence a pure liquid would furnish a straight line graph parallel to the abscissæ, but Sibree's emulsions gave graphs as illustrated in Fig. 28. Thus his results definitely confirm that the viscosity of the emulsions employed vary with the velocity gradient, becoming constant, or nearly so, above a certain velocity gradient. Ageing, up to twenty-eight days, only very slightly influenced the quantitative data obtained.

Varying the viscosity of the internal phase by using limpid and viscous paraffin respectively, so that such viscosities were in the ratio 1 : 38, the resulting emulsions had viscosities in the ratio 1 : 1·4. This supports Hatschek's original contention [4] that the viscosity of an emulsion

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[1] *Ibid.*, **26**, 26 (1930) ; **27**, 161 (1931). See Porter, *ibid.*, **26**, 233 (1930).

[2] See p. 334.

[3] See p. 332.

[4] The best confirmation of this contention is found in the case of bitumen emulsions Gabriel, " Technical Aspects of Emulsions " (London, 1935), p. 140.

TABLE 19

THE VISCOSITY OF AN EMULSION IN RELATION TO VELOCITY GRADIENT

T. Time of 1 Rev. in Seconds.	$\alpha \frac{360°}{T}$. Velocity Gradient.	η'/η_e. Relative Viscosity of Emulsion.	η'. Viscosity of Emulsion in Centipoises.
4200	0·086	51·3	53·2
1160	0·31	31·1	32·2
360	1·0	17·5	18·2
175	2·06	14·5	15·05
102	3·5	12·6	13·1
68·5	5·26	12·2	12·7
53·0	6·8	11·6	12·03
40·4	9·0	11·5	11·95
30·25	11·8	11·0	11·4
28·5	12·6	10·9	11·3
24·3	14·8	11·1	11·5
19·2	19·7	10·8	11·2
13·06	27·6	10·4	10·8
9·9	36·2	10·1	10·5
8·6	42·0	9·9	10·27
8·0	45·0	9·5	9·85

depends, not on the viscosity of the internal phase, but on its volume in the emulsion. Further, to elucidate this point, Sibree prepared emulsions

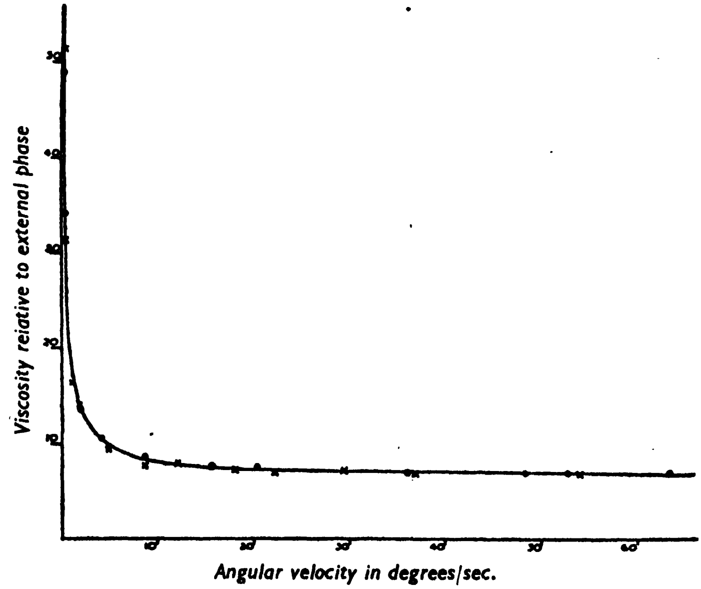

FIG. 28. Viscosity of 50 per cent. paraffin oil/1 per cent. soap solution emulsion in relation to the angular velocity (Sibree).

of limpid paraffin varying the concentration. His results are reproduced in Table 20.

TABLE 20

VISCOSITY OF EMULSIONS IN RELATION TO CONCENTRATION

Concentration of Internal Phase (per cent.).	ϕ	Observed Relative Viscosity. η'/η_e.	Calculated Relative Viscosity. $\frac{\eta'}{\eta_e} = \frac{1}{1-\sqrt[3]{\phi}}$
50	0·5	7·0	4·85
60	0·6	15·23	6·38
68·2	0·682	40·30	8·35
75	0·75	94·5	10·94

If now the percentage volume of the internal phase be calculated from Hatschek's equation, written as $\phi = \frac{(\eta' - \eta_e)^3}{\eta'^3}$, it is found that the ratio $h = \frac{\phi \text{ calculated}}{\phi \text{measured}}$ = about 1·3, provided the actual value of ϕ is $> 0 \cdot 5$. "If we assume the formula to be correct, these figures indicate that the active volume of the disperse phase is throughout about 30 per cent. greater than that of the paraffin itself. If this increase is caused by an adsorption layer, it is obvious that it cannot be of uniform thickness on all particles, but must be thicker on the larger particles, all radii being increased by about 10 per cent.", a condition not easily conceived. Just why the *volume* rather than the *interfacial area* of the internal phase is involved is, therefore, open to investigation.

Sibree's next experiments took account of the size of the globules, as the value of h might possibly be related to this factor. He employed "coarse" emulsions containing globules up to 450μ, and "fine" emulsions containing globules up to 20μ diameter. His viscosity results are summarised in Table 21, based on two tables in his paper.

It is apparent that the fine emulsions are more viscous than the coarse emulsions at equivalent values of ϕ, the difference increasing as ϕ is increased. This fact, of course, is everyday experience with technical emulsions, especially when an homogeniser is employed.

Sibree suspected air entrainment in his emulsions, and actually found 1·4 per cent. of air by volume. Emulsions prepared with the aid of a Viscoliser (see p. 393) enabled dispersions to be obtained wherein no globules exceeded 8μ diameter and 90 per cent. of the globules were below 2μ diameter. The Viscoliser does not entrap air. Although the grain-size of these emulsions was so very different from the previous emulsions, the viscosity of such fine dispersions at the lower concentrations differed little from that of the coarse emulsions. To some extent the absence of air accounts for this agreement, an opinion shared by Narayanaswamy and Watson [1] dealing with the viscosity of petrol-water

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[1] *J. Indian Inst. Sci.*, **17A.**, (vi.), 75 (1934).

TABLE 21

VISCOSITIES OF COARSE AND FINE EMULSIONS

	Percentage of Oil.	η'/η_s (Measured).	ϕ (Measured).	ϕ (Calculated).	h	Diameter of Globules (measured).
	Limpid Paraffin					
Coarse Emulsions	50	7·2	0·50	0·639	1·28	—
	60	16·4	0·60	0·828	1·38	—
	68·2	26·4	0·682	0·890	1·30	220μ down to 20μ.
	75	78	0·78	0·962	1·28	
	Viscous Paraffin					
	48	9·3	0·48	0·711	1·48	—
	57·6	18	0·576	0·786	1·36	—
	65·6	33	0·656	0·912	1·39	340μ down to 20μ.
	75·3	79	0·753	0·962	1·28	
	Limpid Paraffin					
Fine Emulsions	50	8·6	0·50	0·690	1·38	No globules exceeding 10μ.
	55	12·8	0·55	0·784	1·42	
	57·6	19·0	0·576	0·850	1.48	
	69·2	190	0·692	0·984	1.42	
	72	900	0·72	0·997	1·40	
	75	Thick				

emulsions. However, the experiments of Leviton and Leighton,[1] though confirming that the viscosity of emulsions (containing milk fat) does not vary within the limits of experimental error with variations in the degree of dispersion of the fat phase, are attributed to the fact that in such emulsions *the actual volume of the fat phase is not measurably amplified by the association with the fat phase of a portion of the continuous medium.* These authors give data to show that emulsions containing 10 per cent. and 30 per cent. fat respectively do not change their viscosities when the globules are reduced from 3μ to 0·7μ diameter.

Sibree has emphasised that his data were obtained with emulsions wherein the aqueous external phase was confined to Na oleate solution. Conceivably "the value of the volume factor (h) may be specific for a given emulsifier and concentration." That the nature of the emulsifying agent does influence the viscosity of emulsions is generally accepted. Thus Whitmore and Linehan,[2] in their work on essential oil emulsions, reported that agar or gum tragacanth gave rise to more viscous emulsions than did gelatin or gum arabic. Similar observations have been made by Smith and Hazley,[3] whilst Blow [4] observed that the viscosity of rubber latex depends to a large extent on the viscosity of the serum.

Particular attention to this factor has been given by Wilson and Parke [5] in a paper entitled : Some Effects of Emulsifier Concentration on Globule Size and Viscosity in Emulsions.

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[1] See p. 162.

[2] *Ind. Eng. Chem.*, **21**, 878 (1929).

[3] *Quart. J. Pharm. Pharmacol.*, **3**, 362 (1930).

[4] *Trans. Faraday Soc.*, **25**, 458 (1929).

[5] *Quart. J. Pharm. Pharmacol.*, **9**, 188 (1936).

The most recent work in this field is by Broughton and Squires[1] who used seven types of emulsions, with sodium oleate, saponin and triethanolamine oleate (1, 2, and 3 per cent. by weight, respectively) as continuous phases, and Nujol, benzene, and olive oil as the disperse phases. To prevent creaming, all the oils were weighted with α-bromonaphthalene to a specific gravity of 1·00. Intermittent stirring was with a high-speed electric stirrer. Air was removed by a vacuum apparatus, the Briggs homogeniser.[2] Viscosities were measured with the MacMichael instrument.

The conclusions reached were that :—

1. The viscosity of a concentrated emulsion is a function of the rate of shear, approaching an asymptote as the rate of shear is increased. Over wide ranges the relation between shearing stress and rate of shear is linear. For a given emulsion, *i.e.*, a given phase pair and stabiliser concentration (based on the dispersing medium), the limiting viscosity at infinite rate of shear increases with the volume concentration of the disperse phase[3] The quantitative relation between the concentration and the limiting viscosity is best represented by a modified form of the Richardson equation. The Hatschek equation, as modified by Sibree, does not apply.

2. Other than volumetric concentration, the type of stabiliser employed seems to be the variable of most significance in determining the magnitude of the viscosity of any phase pair. Stabilisers producing the best emulsification give emulsions of the lowest limiting relative viscosity.

The authors' results are collected in Table 22 where the *yield point* refers to the point of intersection of the torque axis, when the R.P.M. deflection curves are extrapolated to low rates of shear. It represents the theoretical distorting force necessary to initiate flow. The *limiting viscosity* is the asymptote of the viscosity rate of shear curve or viscosity at infinite shear. The *relative limiting viscosity* is the ratio of the limiting viscosity to the viscosity of the continuous phase.

Inspection of column 3 of Table 22 shows that the yield point as defined above varies even more widely with concentration than does the limiting viscosity. It is well known that relatively dilute emulsions behave like true liquids, showing no yield point and hence no variation in viscosity with rate of shear. Above a fairly definite concentration however, the viscosity becomes a function of the rate of shear and a yield point develops. All the emulsions studied were in a concentration range well above this limit, with the exception of the benzene-triethanolamine oleate emulsion. This emulsion showed no yield point up to a volume concentration of 0·70. In Table 23 are listed the estimated concentrations at which a yield point appeared, obtained by linear extrapolation of the yield point-concentration curve. The third column of Table 23 also shows the limiting relative viscosity of the emulsion at this concentration.

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[1] *J. Phys. Chem.*, **42**, 253 (1938).

[2] *Ibid.*, **19**, 223 (1915).

[3] See also Bredée and de Booys, *Kolloid Z.*, **91**, 39 (1940).

TABLE 22

SUMMARY OF CALCULATED DATA

EMULSION	VOLUME PER CENT (OIL)	YIELD POINT	LIMITING VISCOSITY	RELATIVE LIMITING VISCOSITY
			centipoises	
Nujol-sodium oleate				
4	50	1.94	8.94	9.09
2	60	5.0	14.75	15.0
8	70	84.0	29.9	30.4
3	75	178.5	37.5	38.15
Nujol-saponin				
5	50	0.54	10.97	10.97
6	60	5.0	36.3	36.3
9	70	440	78.5	78.5
7	75	838	143.8	143.8
Nujol-triethanolamine oleate				
10	50	2.9	10.97	2.31
11	60	8.0	18.85	3.98
12	70	83.0	32.45	6.87
27	80	1320	92.3	19.5
Benzene-triethanolamine oleate				
14	50		8.02	1.70
15	60		12.07	2.55
16	70		32.10	6.78
26	75	27.5	66.5	14.05
Benzene-sodium oleate				
20	50	0.97	9.05	7.95
21	60	4.0	14.13	12.42
22	70	36.0	25.2	22.1
Olive oil-triethanolamine oleate				
17	50	24	22.95	4.85
18	60	50	60.30	12.72
Olive oil-sodium oleate				
24	50	0.32	8.90	7.82
24	55	8.0		20.9

Argument is advanced that the yield point is a function of the type of stabiliser and limiting viscosity of the resulting emulsion. Accordingly, if at one volumetric concentration, the yield point and limiting viscosity were known together with the limiting relative viscosity, the viscous behaviour over a wide range of concentrations could be quantitatively predicted.

No generalisations could be made as to the influence of the viscosity of the internal phase on the resulting viscosity of the emulsion. Inspection of the curves obtained from the experimental data shows that the viscosities of emulsions at the same volumetric concentration and for the same stabiliser are in the order of the viscosities of the disperse phases. However, this relation is reversed for the benzene and Nujol emulsions at 75 volume per cent. Again, the olive oil and benzene

TABLE 23

VOLUME CONCENTRATION AND VISCOSITY AT INITIAL YIELD POINT

EMULSION	VOLUME CONCENTRATION AT WHICH YIELD POINT APPEARS	CORRESPONDING LIMITING RELATIVE VISCOSITY, η_r
		centipoises
Nujol–sodium oleate	0.437	5.5
Nujol–saponin	0.489	11.0
Nujol–triethanolamine oleate	0.440	1.65
Benzene–triethanolamine oleate	0.718	8.7
Benzene–sodium oleate	0.465	6.0
Olive oil–triethanolamine oleate	0.407	1.8
Olive oil–sodium oleate	0.445	6.0

stabilised by sodium oleate, the viscosities of the more concentrated emulsions are in the order of the viscosities of the disperse phases, but at 50 volume per cent. the viscosities of the two emulsions are identical.

As regards the effect of the stabiliser, it is obvious that for a given phase pair the limiting relative viscosity at a definite concentration varies widely with the type of stabiliser used. The variation in viscosity at the same concentration is in the order of increasing ease of emulsification, the most efficient stabiliser producing the emulsion of lowest viscosity. Thus, triethanolamine oleate emulsified Nujol practically spontaneously, but the saponin emulsion was quite difficult to prepare. The definite function of the stabiliser is best seen in the case of 70 volume per cent. emulsions with Nujol, there being a thirteen fold variation for the relative viscosities when saponin triethanolamine oleate were employed.

Since there are emulsifying agents which (*a*) reflect the influence of the *p*H value (*e.g.*, gelatin),[1] (*b*) readily form even visible interfacial films,[2] (*c*) are used as solid powders [3] and (*d*) give the unexpected type of emulsion,[4] it is obvious that much research is still required into the general question of the viscosity of emulsions. With certain emulsifying agents, alteration of the volume concentration of the internal phase may lead to abrupt change in the viscosity of the system due to the inversion of the emulsion, a phenomenon investigated by Parke and Graham.[5]

Sumner's method of preparing emulsions should prove useful, since air cannot be entrapped and, moreover, fairly homogeneous dispersions are somewhat accurately controllable.[6]

Complex emulsion systems like milk [7] and cream make viscosity studies very difficult. Thus, cream is not truly viscous, exhibiting thixotropic character.[1] Ageing increases the viscosity and agitation reduces it. Again, creams of the same fat content show quite different viscosities.

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[1] Friedman and Evans, *J. Am. Chem. Soc.*, **53**, 2898 (1931); Zhukov and Bushmakin, *J. Russ. Phys. Chem. Soc.*, **59**, 1061 (1927).

[2] Serrallach *et al*, *Ind. Eng. Chem.*, **23**, 1016 (1931); **25**, 816 (1933).

[3] See p. 138.

[4] Holmes, *J. Am. Chem. Soc.*, **47**, 323 (1925).

[5] *J. Chem. Soc.*, **1933**, 1214.

[6] *J. Phys. Chem.*, **37**, 279 (1933).

[7] Tapernoux and Vuillaume, *Lait*, **14**, 449 (1934); *Compt. rend. soc. biol.*, **115**, 1128 (1934); Kobler, *Arch. Gesamt. Physiol.*, **125**, 1—72 (1908); Leighton and Leviton, *J. Phys. Chem.*, **36**, 523 (1932); Nokayama, *Mitt. Med. Akad. Kioto*, **4**, 154 (1930).

VISCOSITY OF WATER-IN-OIL EMULSIONS

Apparently the first serious investigation concerning the viscosity of water-in-oil emulsions is due to Sibree. His oil phase was a mixture of olive oil and bromoform, equal then to water in density. The emulsifying agent was 1 per cent. of Schou's oil (see p. 125), dissolved in the warmed oil phase. Water from a burette was slowly added to the warm oil, both phases being at the same temperature, and emulsification was effected by Briggs' method of intermittent agitation (see p. 334). In this way it was quite easy to prepare systems containing 70 per cent. of water as globules.

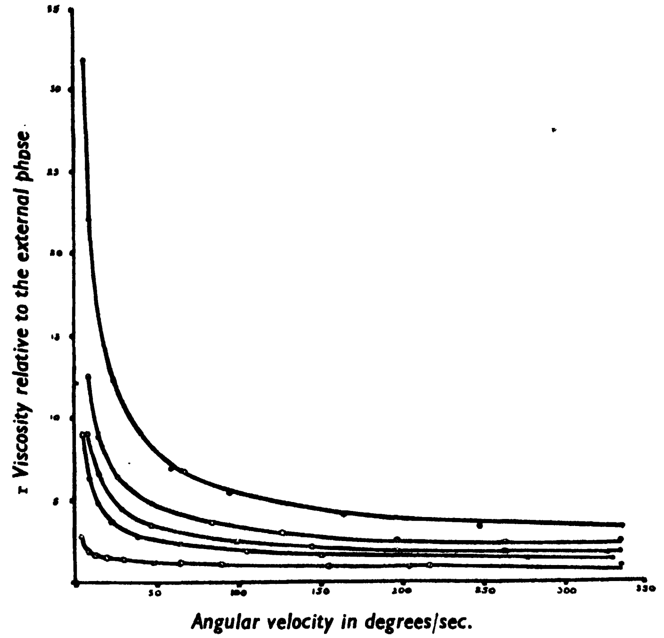

FIG. 29. Viscosity—angular velocity curves for W/O emulsions (Sibree).

Fig. 29 gives a family of curves showing the relationship between the viscosity of the emulsion and the angular velocity of the outer cylinder of the viscometer for various concentrations of the emulsion. Table 24 gives these results tabulated, the value of the viscosity being taken (as previously) at the end point. It should be noted that the viscosity of the oil was of the same order as that of a 60 per cent. sucrose solution.

From this table it will be seen that these emulsions agree with Hatschek's formula when the volume is corrected by the hydration factor h. This may be considered satisfactory in view of their high viscosity.

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[1] Nair and Mook, *J. Dairy Sci.*, **16**, 1 (1933). See also: Babcock, U.S. Dept. Agric., *Tech. Bull.*, **249**, 1–19 (1931); Lyons and Pyne, *Econ. Proc. Roy. Dublin Soc.*, **2**, 461 (1933).

TABLE 24

VISCOSITY OF A COARSE W/O EMULSION

Water per cent.	η'/η_e (Measured).	ϕ (Measured).	ϕ (Calculated).	h	Diameter of Globules.
50·0	8·4	0·500	0·677	1·35	Between 3μ and 100μ.
54·7	11·9	0·547	0·767	1·40	
59·7	16·1	0·597	0·824	1·38	
65·3	22·2	0·653	0·850	1·30	
70·0	32·7	0·700	0·912	1·30	

Oil-in-water emulsions have special significance in petroleum technology and the viscosity factor is important from the point of view of lifting to the surface from the wells, handling and transport. Monson[1] has accordingly made an investigation of the viscosity ratios (emulsion viscosity relative to clean oil viscosity) for twenty emulsions prepared from five California crude oils, using four different phase-volume ratios at three temperatures. The *viscosity ratio* was determined because the Einstein and Hatschek formulæ gave results divergent from the actual measured viscosities.

No specified emulsifying agents were used, the crude oils and water being emulsified by means of a piston type apparatus. Table 25 from the author's paper collects the results obtained. The maximum viscosity ratio to be expected in emulsions of any of the crude oils tested is approximately 1·3 for those containing 10 per cent. water, and 1·8, 2·7, and 4·1 for those containing 20, 30 and 40 per cent. water respectively. In general, the increase in temperature required to reduce the viscosity of an emulsion to that of the clean oil at 100° F. did not exceed approximately 2° F. for each per cent. of water present.

THE DIELECTRIC CONSTANT OF EMULSIONS

The dielectric constant may be defined[2] " as a measure of the work done by an external field in orienting molecules against the effect of their thermal agitation." With polar liquids over a certain range increasing the frequency causes a decrease in the dielectric constant, such frequency range being related to the dimensions of the orienting molecule and the viscosity of the medium, the latter bringing about frictional losses in rotation.

The size and weight of electrically dissymmetrical particles, dissolved or suspended in a liquid, can be estimated from the critical frequency of alternating current above which the dielectric constant decreases with increase in frequency.[3]

Various formulæ have been derived to express the dielectric constant

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[1] *Ind. Eng. Chem.*, **30**, 1287 (1938).

[2] Williams and Oncley, *J. Rheol.*, **2**, 271 (1931). Recently, Heymann, *Kolloid-Z.*, **66**, 229, 358 (1934), has presented an extensive review on the dielectric constants of colloid systems.

[3] Marinesco, *Compt. rend.*, **189**, 1274 (1929); *J. chim. phys.*, **28**, 51 (1931); *Kolloid-Z.*, **58**, 285 (1932); Weber, *Z. Physik.*, **70**, 711 (1931); Williams and Oncley, *Physics*, **3**, 314 (1932); Cole, *Trans. Faraday Soc.*, **33**, 966 (1937).

TABLE 25

VICOSITIES AND VISCOSITY RATIOS OF PREPARED EMULSIONS

Per Cent Water	Unit[a]	East Coyote			Midway-Sunset (Taft)			Olinda			Round Mountain			Signal Hill		
		100° F.	130° F.	185° F.	100° F.	130° F.	185° F.	100° F.	130° F.	185° F.	100° F.	130° F.	185° F.	100° F.	130° F.	185° F.
0	*s*	664	286	95.0	1247	474	122	345	160	67.4	807	304	90.3	424	196	78.8
	k	144	61.8	20.5	270	102.4	26.3	74.7	34.6	14.5	175	65.7	19.4	91.8	42.3	17.0
	a	133	56.6	18.3	253	94.9	23.9	68.8	31.5	12.9	164	60.9	17.6	84.4	38.5	15.1
10[b]	*s*	853	376	119.6	1521	568	151	456	211	85.0	1034	397	111	602	274	99.3
	k	185	81.3	25.7	329	123	32.5	98.7	45.6	18.3	224	85.8	23.9	130	59.2	21.4
	a	173	75.1	23.2	311	114.5	29.7	91.5	41.8	16.4	211	79.9	21.8	124	54.3	19.2
	VR	1.30	1.33	1.27	1.23	1.21	1.24	1.33	1.33	1.27	1.29	1.31	1.24	1.47	1.41	1.27
20	*s*	1241	524	166	2331	838	210	611	292	104.5	1439	551	144	811	360	126
	k	269	113	35.8	505	181	45.2	132.3	63.1	22.5	311	119	31.0	176	77.8	27.1
	a	252	105	32.5	479	170	41.5	123.5	58.2	20.3	295	111	28.4	164	72.0	24.6
	VR	1.90	1.86	1.78	1.89	1.79	1.74	1.80	1.85	1.57	1.80	1.83	1.61	1.95	1.87	1.62
30	*s*	1940	780	240	3337	1224	319	906	456	152	2106	794	181	1289	540	184
	k	420	169	51.7	722	264	68.7	196	98.5	32.7	456	172	39.0	279	117	39.6
	a	397	157	47.2	705	249	63.3	184	91.5	29.7	434	161	35.9	263	109	36.1
	VR	2.98	2.77	2.58	2.78	2.62	2.65	2.68	2.91	2.31	2.65	2.65	2.07	3.14	2.83	2.39
40[c]	*s*	2744	1168	367	5017	1835	468	1464	683	(230)[d]	3254	1120	240	1840	834	286
	k	594	252	79.0	1086	396	100.8	317	148	49.5	704	242	51.7	398	180	61.6
	a	565	237	72.6	1040	375	93.3	300	138	45.4	674	229	47.8	379	169	56.6
	VR	4.24	4.19	3.97	4.10	3.95	3.91	4.36	4.39	3.53	4.11	3.76	2.71	4.49	4.41	3.75

[a] *s* = Saybolt Universal viscosity, seconds; *k* = kinematic viscosity, centistokes; *a* = absolute viscosity, centipoises; *VR* = viscosity ratio.
[b] Midway-Sunset (Taft) emulsion is 9.2% water; Round Mountain, 10.9%; Signal Hill, 10.4%.
[c] Round Mountain emulsion is 41% water. [d] Taken from viscosity-temperature curve (observed value low).

of a mixture as an additive function of the dielectric constants of the constituents. Such formulæ take the general form :

$$f(\epsilon) = \delta_1 f(\epsilon_1) + (1 - \delta) f(\epsilon_2).$$

Where ϵ = dielectric constant of the mixture.

ϵ_1 and ϵ_2 = dielectric constant of the two constituents.

δ = the volume concentration of the constituent possessing dielectric constant ϵ_1.

f = expresses " function of."

Emulsions, with their dispersed spherical particles, are especially suitable for investigation, and extensive experiments have been conducted by Piekara.[1]

Using emulsions of water in transformer oil, ethyl alcohol and water in paraffin oil, and mercury in paraffin oil, the concentration of internal phase being between 0·0002 and 0·0005, it was found that :

(*a*) with ϵ_1 and ϵ_2 constant and globule radius (μ) constant, the value of ϵ is about 70 per cent. greater than that calculated from the Lorenz-Lorentz formula :

$$\frac{\epsilon - 1}{\epsilon + 2} = \delta \frac{\epsilon_1 - 1}{\epsilon_1 + 2} - (1 - \delta) \frac{\epsilon_2 - 1}{\epsilon_2 + 2}.$$

and thus ϵ depends on the volume concentration, δ, much more than the formula demands, and is not linear for low concentrations, as would be expected from the formula :

(*b*) When ϵ_2, δ, and μ are constant, the value of ϵ depends upon that of the internal phase, ϵ_1, more than the Lorenz-Lorentz equation anticipates :

(*c*) The value of ϵ increases with the finer dispersion of the emulsion, so that ϵ must be expressed as a function of μ ; accordingly, $\epsilon = f(\epsilon_1, \epsilon_2, \delta, \mu)$.

Assuming that the divergence between observed and calculated values in the foregoing might be due to the employment of mobile emulsions, Piekara [2] then employed an emulsion of mercury in vaseline, thus eliminating the movements of the globules. The results obtained accorded with those reported in the earlier investigation. No appreciable effect on the value of ϵ could be attributed to interfacial tension, or to the electric charge on the globules. Further experiments [3] using mercury-in-vaseline emulsions, showed that, in contrast to mobile emulsions, the value of ϵ is practically a linear function of δ. Piekara, therefore, postulates that in the mobile emulsions the electric charges on the globules of the internal phase exercise an orientating influence on the dipolar molecules of the internal phase and so reduce the value of ϵ.

Later extension of his investigations [4] dealt with the relation of ϵ to the dispersity of the emulsion, particularly in regard to the influence of the interface layer, this depending on the radii of the globules.

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[1] *Bull. intern. acad. Polonaise* (1928), 201.

[2] *Loc. cit.*, (1928), 223.

[3] *Kolloid-Z.*, 49, 97 (1929) ; *Physik. Z.*, 31, 579 (1930).

[4] *Kolloid-Z.*, 58, 283 (1932) ; cf. Urbanski, *Acta. Phys. Polon.*, 1, 165 (1932) and reply by Piekara, *ibid.*, p. 285 ; Zhuravlev, *J. Phys. Chem.* (*U.S.S.R.*), 5, 784 (1934).

Neglecting the influence of the interface layer, the value of ϵ may be calculated from the Clausius-Mosotti equation for very diluted emulsions :

$$\frac{\epsilon - \epsilon_2}{\epsilon + 2\epsilon_2} = \delta \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}.$$

Two cases were considered :—

(A) *Emulsions in liquids of low dielectric constant.* Alcohol + water-in-paraffin. Plotted $\Delta\epsilon$ against δ, where $\Delta\epsilon$ = difference between ϵ and ϵ_2 (value for the pure medium). Besides the "interfacial layer effect," one can separate an effect manifested in an inclination of the graphs from the linear, so that many measured values of $\Delta\epsilon$ are smaller than those calculated from the linear. He takes this to signify that the charged globules bring about to some extent orientation of the adjacent dipoles of the internal phase.

(B) *Emulsions in liquids of high dielectric constant* such as paraffin-in-ethyl alcohol + water, both phases of S.G. 0·850 at 15° C., $\epsilon_1 = 2{\cdot}13$ and $\epsilon_2 = 34{\cdot}76$.

To find the effect of the degree of dispersion on ϵ, emulsions were employed : (*a*) five of coarse character, with globules of diameter 1 to 400 μ ; (*b*) four of fine dispersion, 0·7 to 70μ ; (*c*) two with globules of diameter 1 to 80 μ. The graph obtained by plotting $\Delta\epsilon$ as ordinate and ϵ as absicissa was a straight line. The surprising result is established that the deviations from the Clausius-Mosotti law are relatively much smaller than in the case of the water/oil emulsions, which naturally possess a much feebler dipole character. The lowering of ϵ, as a consequence of the dipole effect, is now not significant, and its dependence on the grain-size of the emulsion scarcely evident. When one compares the measured and the calculated values of $\Delta\epsilon$ for different globule sizes, particularly for the more concentrated emulsions, it can be assumed that ϵ is somewhat greater, the smaller the globules. Piekara's opinion, therefore, is that the " interface effect " and the " dipole effect " act in opposite directions, although too small to measure. His latest publication [1] deals with the interfacial layer, and he states that the dependence of the dielectric constant of emulsions on the degree of dispersion is a question of the processes taking place in the interfacial layer. Such can be, (*a*) in the interfacial layer the molecules are in an entirely different molecular environment than in the interior of the liquid concerned ; (*b*) if the molecules do not possess spherical symmetry, they arrange their axes in the separating layer in regular fashion ; (*c*) in the majority of emulsions, adsorption of emulsifying agent occurs at the interface, so profoundly affecting the value of ϵ.

Piekara [2] has also used the measurement of dielectric constant to study the behaviour of mixtures of liquids in the neighbourhood of the critical point. With hexane/nitrobenzene, the critical temperature of dissolution is 16·9° C., and the critical concentration 51·4 per cent. Piekara tested the behaviour of the dielectric constant ϵ, the density d, the gram polarisation of the mixture Pgr, and the molecular polarisation P of the dissolved nitrobenzene, when approaching the critical point where the considerable fluctuations of density cause the critical opalescence.

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[1] *Kolloid-Z.*, 59, 12 (1932).

[2] *Phys. Rev.*, 42, 448 (1932) ; *Bull. acad. Polon.*, (1933), 319 ; for estimating the composition of emulsions by measuring the dielectric constant by an ohmic resistance apparatus, see : Schönberg and Glück, Ger. Pat., 639,889 (1936).

As the temperature decreases to the critical temperature, the dielectric constant increases, though at a decreasing rate. Critical opalescence sets in at 18·7° C., but even above this temperature apparently-free from opalescence the very feeble fluctuations in density result in decreased polarisation. At 16·9° C. where phase separation occurs, a rapid increase in dielectric constant is shown, due to the formation of an emulsion of hexane-in-nitrobenzene. Formation of the opposite emulsion, nitrobenzene-in-hexane, brings about a rapid fall in the dielectric constant.

The physiological consequences of high frequency fields have been mentioned by Marshall,[1] who measured the heat gained by emulsions exposed to such fields. Employing emulsions of cotton-seed oil with CCl_4 (5 : 1) in 1 per cent. sodium oleate solution (the two phases thus possessing equal densities), the phase volume ratio being 1 : 1, he found "the absorption in liquid dielectrics is a function of potential gradient (field intensity) as well as frequency, and that for values of potential gradient above at least 70 volts per millimetre, the rate of rise of temperature-frequency curve increases rapidly with frequency." Very high absorption values were exhibited for the emulsions, due to their colloidal structure. There is also the possibility that the energy is dissipated at the oil/water boundaries.

The dielectric properties of water-dielectric interphases have been investigated by Fricke and Curtis [2], who point out that when a dielectric dispersed in water is placed in an electric field, a part of the current passes through the system at the interphases and these become polarised. Hence the dielectric properties of such systems are generally different from what would be expected from the contributions of the single phases, on the basis, for example of the Clausius-Mosotti-Maxwell theorem, for the particular case of a suspension of spherical particles. This influence of the interphases is especially pronounced when measurement is made with direct current or with alternating current of low frequency, in which case the dielectric properties may be radically different from those of either of the components, as measured in bulk.

The argument developed is that a unit element of interphase should generally be characterised by two complex admittances, for the directions parallel to, and perpendicular to, the interphase respectively. With the suspensions studied the latter influence was negligible whilst the former was expressed in terms of interphasial conductivity and interphasial capacity, which decreases and increases respectively as the frequency decreases.

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[1] *J. Gen. Physiol.*, **13**, 637 (1930).

[2] *J. Phys. Chem.*, **41**, 729 (1937).

ELECTRICAL CONDUCTIVITY OF EMULSIONS

Since an oil is an insulator, it is to be anticipated that whilst O/W emulsions will conduct an electric current, W/O emulsions will not ordinarily do so. This is, in fact, a criterion for determining emulsion type as proposed by Clayton.[1]

Little work has been published on the mathematical treatment of the electrical conductivity and capacity of disperse systems, Fricke [2] has discussed the electrical conductivity of a suspension of homogeneous spheroids, later, in association with Morse,[3] testing his conclusions experimentally with cream.

The subject has importance in biology. The interior of a biological cell is a well-conducting salt solution, but at its surface polarisation or the presence of a non-conducting membrane obstructs the passage of an electric current with a resulting low conductivity and high dielectric constant for the system. Again determination of the electrical conductivity of a suspension may yield a method whereby the volume concentration of the suspension may be obtained, knowing the specific conductivities of the two phases. Cream may be cited in illustration. The formula employed is :

$$\frac{k - k_1}{k + 2k_1} = \phi \frac{k_2 - k_1}{k_2 + 2k_1},$$

where : k = the conductivity of the suspension,
k_1 = ,, ,, ,, ,, continuous phase,
k_2 = ,, ,, ,, ,, disperse phase,
ϕ = the volume concentration of the disperse phase.

In the case of non-conducting spheres employing specific resistances instead of conductivities, there results :

$$\frac{r - r_1}{2r + r_1} = \frac{\phi}{2}.$$

The formula has been confirmed by Millikan [4] with emulsions of water in benzene + chloroform, for volume concentrations up to 15 per cent.

Fricke has pointed out that the usual derivation of the formula leads to the conclusion that it only holds for dilute systems, since the electric field around a suspended particle due to the presence of electric charges on the other suspended particles is taken as equal to the average value of this field over the entire space of the suspended medium. Whilst it may be difficult to decide whether the formula holds strictly when there is random distribution of the suspended particles, certain data such as the values of the refractive index of the system indicate a very close accord. Therefore, Fricke's presentation includes the interaction of the suspended particles, adding "to the original field value the mean value of the forces due to the charges on the suspended particles throughout the whole space of the suspending medium." Experimental verification of the formula proves the exactness of this method.

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[1] See p. 462.
[2] *Phys. Rev.*, **24**, 575 (1924); *J. Gen. Physiol.*, **6**, 375, 741 (1923—1924); *Physics*, **1**, 106 (1931); *Symposia on Quant. Biology*, **1**, 117 (1933); Fricke and Curtis, *J. Phys. Chem.*, **41**, 729 (1937).
[3] *Phys. Rev.*, **25**, 361 (1925).
[4] *Wied. Ann.*, **61**, 337 (1897).

Diluting a heavy cream with the skim milk originally separated therefrom gave a series of creams of varying fat concentrations. Conductivities were measured with a Wheatstone bridge, employing a substitution method, with frequencies of the order of 83,000 cycles per second. Stirring influenced the results, a continuous and somewhat rapid increase in resistance being noted when stirring ceased. Probably stirring induces ordered array of the fat globules. Again, with increase in frequency, a decrease in resistance is manifested, no doubt due to a polarisation resistance at the conductivity cell electrodes.

The following table by Fricke and Morse compares the values for ϕ calculated from the conductivity data for each dilution with those obtained by dividing the value of ϕ for the lowest cream as standard by the respective dilution factors. Although selected data are given, equally as good agreement obtained for the range of values of ϕ from 8 to 62 per cent.

TABLE 26

TEST OF FORMULA FOR CONDUCTIVITY OF SUSPENSIONS

	Volume Concentration (per cent.).	
	Calculated from Resistances.	Calculated from Dilution Factors.
Primary cream . . .	62·73 ± 0·12	62·93 ± 0·19
Dilution No. 1 . . .	40·40 ± 0·08	40·44 ± 0·12
Dilution No. 2 . . .	22·49 ± 0·06	Standard

There is a paucity of data on the electrical conductivity of emulsions and attention seems mainly to have been devoted to milk,[1] where K_{15} = 0·0035 to 0·0047, lying usually at 0·0040 to 0·0042. There is a marked correlation between conductivity and the chloride content of milk.[2] The non-conducting fatty portion of milk, by obstructing the passage of ions, reduces the electrical conductivity of the named serum. Thus, Taylor [3] observed an increase of 11·4 per cent. in the conductivity of the milk, when the 5 per cent. of fat was removed. Wardlaw's data showed a similar result.[4] Palmer [5] used the electrical conductivity of cream to investigate churning, and found that as churning progressed, the resistance gradually increased until, after about 105 minutes, a maximum resistance was reached; after a stationary period of about 30 minutes, the resistance began to decrease, at first slowly and then very rapidly. Coincident with the separation of butter masses, the resistance became substantially that of the butter milk.

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[1] Krenn, *Milchwirtschaft Forsch.*, **14**, 513 (1933); Jackson and Rothera, *Biochem. J.*, **8**, 1 (1914); Roadhouse and Koestler, *J. Dairy Sci.*, **12**, 426 (1929).

[2] Coste and Shelbourn, *Analyst*, **44**, 158 (1919).

[3] *J. Proc. Roy. Soc. N.S. Wales*, **47**, 179 (1913).

[4] *Proc. Linnean Soc. N.S. Wales*, **43**, 613 (1918).

[5] *Colloid Symposium Monograph*, **1**, 411 (1923). See p. 433.

Dixon and Bennet-Clark[1] have carried out interesting experiments relating to the electrical properties of oil/water emulsions, with particular reference to antagonistic emulsifiers and the critical point. Working with emulsions of olive oil in water + sodium oleate, the electrical conductivity was examined for the effect of the relative volumes of the phases. It was found that when the ratio water : oil was greater than 45 : 55, the resistance is independent of the ratio; however, further decrease of the water phase brought about a more and more rapid rise of the resistance of the emulsion, which asymptotically reached infinity when the water content was about 3 per cent. Such increased resistance was traced by means of the microscope to the gradual inclusion of the water within the oil globules (multiple emulsions). The effect of alternating currents on emulsions was striking. An emulsion of olive oil 7 c.c., water 3 c.c., sodium oleate 0·00007 mol., and $CaCl_2$ 0·00003 mol., had an initial resistance of about 5 megohms. Using a conductivity cell with platinum electrodes 2 mm. apart and applying for ½ second an alternating current of 160 volts, 50 cycles, produced an almost instantaneous decrease in the resistance of the emulsion to about 200,000 ohms. Now such an emulsion was of the water/oil type, yet the electric stimulus produced a condition of ionic permeability, followed by slow, sometimes erratic, rise in resistance, several hours elapsing before the original value was recovered. As anticipated, the greater the ratio Ca : Na, the less was the magnitude of the electric response. The appearance of the emulsion, as a thin film, whilst changing in resistance under the influence of an electric current, was carefully noted under the microscope, using electrodes 3 mm. apart and current of 200 volts A.C. The authors record: "At the moment of application of the stimulus to a sensitive film, a series of 'flicks' or explosions appear to take place in various parts of the film. On close examination it is seen that these are due to the sudden coalescence of previously separate water drops or particles of oil/water emulsion to form large masses of water, almost invariably with oil-drops enclosed inside them, and frequently of an elongated shape. In many cases it was observed that the spherical water-drops distributed through the oil suddenly lost their spherical shape on application of the stimulating current. In one case this loss of spherical shape of the water-drops was followed immediately by the separation of the interstitial oil into nearly spherical masses, with the water forming the continuous phase. The effective stimuli appear to act by causing the interfaces originally concave towards the water-phase to become concave towards the oil-phase. So that either partial or, in extreme cases, nearly complete inversion takes place." A further series of experiments concerned four water/oil emulsions passed through an homogeniser. A stock emulsion consisting of 70 volumes olive oil, 30 volumes aqueous N/50 sodium oleate, was mixed with 0·3, 0·4, 0·5, and 0·5 c.c. respectively, of M/10 $CaCl_2$, so that the ratios Na : Ca were 4 : 1, 3 : 1, 2·4 : 1, and 2 : 1, respectively. Their respective specific resistances in megohms were: (A) 1760, (B) 1830, (C) 1540, and (D) 1760, respectively, which decreased on ageing.

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[1] *Nature*, **124**, 650 (1929); *Proc. Roy. Dublin Soc.*, **19**, 422 (1930); **20**, 211 (1932).

The effect of applying alternating current of 50 cycles per second was investigated for one second to a layer of emulsion 1 mm. thick, 24 hours old, and gave the following results.

Resistance.	Emulsion D.		Emulsion A.
	(100 volts).	(195 volts).	(100 volts).
Before stimulus	1010	990	610
2 min. later	960	101	—
3 ,,	—	68	—
5 ,,	—	62	—
8 ,,	—	550	—
13 ,,	—	960	15

These show : (1) the extreme sensitivity of emulsion A to mild electric stimulus, owing to the high ratio of Na : Ca ; (2) when the ratio Na : Ca is low, 2 : 1, (emulsion D), 100 volts effect a negligible change, whilst 195 volts cause a rapid drop in resistance followed by a pronounced recovery. The authors point out that "the characteristic feature of the homogenised emulsions dealt with is that recovery nearly always took place from moderate stimuli." The reason given is that homogenisation avoided multiple emulsions. Application of a current of 195 volts for one second caused the water globules to become ellipsoidal and to arrange themselves in rows of chains roughly parallel with the direction of the electric field. Coalescence of the globules was negligible, and, while the ellipsoidal form was retained for some time after the stimulus, the filaments of globules gradually broke to individuals. "Evidently the formation of narrow filaments of water-phase is responsible for the decrease in resistance, and the recovery to the original high value would seem to be due to the break-up of the filaments of drops into separate drops. A very large stimulus (high voltage or long duration), brings about much coalescence of the droplets of the filaments, and the resulting large drops do not break up again, so the effects of a stimulus which is too large are in general irreversible ; no recovery takes place."

The string-formation of oil globules in milk and cream under the influence of an alternating electric field has been described by Muth.[1] The oil globules form chains the long axis of which lie in the direction of the applied field. Removal of the field caused the re-appearance of the primary globules. Muth believes that due to the electrical double layer at the dineric interface, an alternating polarity is there set up in rhythm with the frequency of the field, the string-formation, however, being independent of the frequency of alternation.

THE STABILITY OF EMULSIONS

Apart from the question of the relative densities of the two phases and the beneficial influence of fine dispersion, the permanence of emulsions depends on the properties of the emulsifying agent, in respect to ageing or to the presence of electrolytes. Rozieres [1] has patented a method for the preparation of vegetable casein, which aptly illustrates this. The oleaginous seeds or press cakes obtained therefrom are ground with alkali solution and the emulsion of oil in casein solution so obtained is treated to adjust the *p*H value between 7·07 and the flocculation point of the casein (about *p*H5). The emulsion is now unstable, and centrifuging removes the oil, whence acidification of the residue precipitates the casein.

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[1] *Kolloid-Z.*, **41**, 97 (1927). Similar observations have been made by Fritz, *Milchwirtschaft Forsch.*, **16**, 476 (1934).

The majority of emulsifying agents undergo no adverse change on ageing the emulsions, although proteins may so denature as to cause a gel structure throughout the system. Salad dressings prepared by the aid of egg white often show this effect, with accompanying separation of the aqueous phase. Soaps apparently depend for their ageing phenomena on the actual concentration of soap present. Harkins and Beeman [2] investigated the stability of such emulsions by a determination of the variation of the distribution of sizes (diameters, areas and volumes) with the time. They found that "the more concentrated soap solutions seem to form emulsions which are very stable even over long periods of time. Emulsions made with 0·1 M soap solutions and with greater concentrations, where the soap is soluble enough to remain in solution, were not observed to change appreciably in the course of a year. At the other extreme, emulsions produced by very dilute soaps were found to change rapidly. Thus, 0·0005 M, 0·0008 M and 0·008 M soaps gave unstable emulsions which showed signs of breaking within a few hours after making."

The work of Harkins and Beeman has recently been extended in an important paper by Miss Berkman [3] who determined the distribution of sizes for emulsions of octane and heavy paraffin oil (Stanolax) in aqueous solutions of Na oleate. Very pure materials were carefully prepared and the determination of globule sizes was made with a Leitz microprojection equipment. (See p. 472.) Number distribution curves were obtained for the two classes of emulsions.

The influence of the concentration of Na oleate, especially affecting changes in the distribution with time, was investigated to ascertain the relation between the size-frequency analysis and the stability of the emulsion. Quite definite were the findings: (1) the maximum number of globules of diameters of 1 to 1·5 μ does not depend on any particular concentration of the Na oleate employed to promote a relatively permanent emulsion, whatever its age (even in years) since its initial preparation; (2) there is somewhat gradual distribution of intermediate size globules; (3) deviations in both directions from the maximum size globules correspond to the peak in the number distribution curve prior to the establishment of a stable static equilibrium of the emulsion, *e.g.*, the course of changes in the distribution of sizes may be compared to the swing of a pendulum at both its extremities; (4) the method enables observations of changes in the distribution of sizes with time due to ageing of the emulsions, the concentration of the soap being a factor therein; (5) of large globules, 10 to 30 μ, only a very small percentage was present in stable emulsions, their incidence indicating a transition to an unstable system; (6) the maximum peak in the distribution curve appeared to undergo no displacement when a viscous oil was used instead of the more fluid one.

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[1] Ger. 522,207 (1930).
[2] *J. Am. Chem. Soc.*, **51**, 1686 (1929).
[3] *J. Phys. Chem.*, **39**, 527 (1935).

Whilst it is undoubtedly fundamental to study emulsion stability on the basis of size-frequency analysis, the practical commercial aspect of stability is the observation of creaming and/or the separation of water and/or oil in the emulsion. Factors involved in this matter are: vibration, head-space of gas, temperature, globule sizes, densities of phases, gelling or other ageing change of the emulsifier.

Lederer[1] has suggested a scheme for expressing separation changes quantitatively. His argument is as follows:—

The separation (of oil or water) of quantity dV in time dt depends in the first place on the time t and the still emulsified portion (1-V), where the original quantity of the phase concerned = 1. This dependence is a simple proportionality. In the second place, dV depends on the height *ab* which the emulsified globules must travel to reach the separation layer and make the separated portion of the phase clear. This height is proportional to V in the case of a cylindrical vessel. However, the sedimentation velocity is not simply proportional to the height, but to a power of this, which can theoretically lie between 0 and 1, and is usually 0·5. Errors of ± 3 per cent. accompany this method of evaluation.

The equation for sedimentation is:

$$\frac{dV}{dt} = k\,(I - V)\,V^{\frac{1}{2}}.$$

The "velocity coefficient" k depends on a series of conditions such as the chemical nature of the two liquids, the size and charge of the globules, the viscosities of the liquids, etc. It also depends on the choice of the time unit. Integration of the equation gives:

$$kt = \log\frac{1 + \sqrt{V}}{1 - \sqrt{V}}.$$

A more useful criterion is the time t at which half of the end volume of separated material is reached. The author gives a table which illustrates good agreement between calculated and determined values for an emulsion of petroleum in a 15 per cent. aqueous solution of commercial Igepon A, but the method of dispersion is not indicated.

A number of patents dealing with bitumen emulsions concern stability. Very viscous emulsions[2] are gained by addition to the aqueous phase of some agent which has marked attraction for the water. The tendency of bitumen emulsions containing soap to break down prematurely in use when mixed with such substances as lamp-black, asbestos or cement is overcome by pre-treatment of these substances with NaOH or Na_3PO_4 before admixture with the emulsion.[1] In the same connection, the rupture of the emulsion is prevented[2] by adding about 0·1 per cent. of an alkali salt of an acid, the Ca salt of which is particularly insoluble in the presence of CO_2, *e.g.*, fluorides, oxalates or fluosilicates of Na. An asphalt emulsion which will withstand hard water is claimed[3] by emulsifying with a mixture of alkali and mineral oil sulphonates.

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[1] *Kolloid-Z.*, **71**, 61 (1935).

[2] Colas Products, Ltd., Gabriel *et al*, Brit. 389,810 (1933); Fr. 738,823 (1932).

An interesting test to determine the stability of certain emulsions stabilised with egg yolk or Irish moss has been described by Myers.[4] It is based on the observation that finely-dispersed stable emulsions when mixed with lethal amounts of bacterial toxins (see p. 261) and incubated for 30 minutes at 37° C. do not kill guinea-pigs. Instability of the emulsion would not afford animal protection as the adsorption of toxin on the globules would be impossible.

An excellent summary has been furnished by King[5] under the title: "Some Factors Governing the Stability of Oil-In-Water Emulsions." The present writer thoroughly endorses King's conclusions and the following account is abridged from King's paper, which deserves careful reading.

Since the globule size progressively increases, emulsions are thermodynamically unstable systems. In some emulsions a slow or a rapid separation of the internal phase leads to a distinct bulk layer, an essentially irreversible process. Commonly, emulsion separation of this type is quite slow and it is not surprising that investigators have sought to find some criterion to measure emulsion stability. However, as King points out, there is no single property of an emulsion other than rate of coalescence or separation of internal phase that can be considered to constitute stability. Here, *creaming* (separation of a layer of *external* phase) must not be confused with instability; indeed, the "cream" may be a very stable system.

While a preliminary study of emulsion stability will be concerned only with the degradation of a system with time, it is important also to recognise and measure the effect of environmental changes, especially temperature and those brought about by the addition of electrolytes. Some of these have already received considerable study which has yielded information fundamental to emulsion theory, but much of this work (and especially that concerning the effect of electrolytes) has been done with oil hydrosols. Generalisations from the study of such systems may be completely misleading.

By far the commonest type of emulsion is that which is stabilised by the presence of an emulsifying agent in sufficient concentration to form at least a unimolecular layer. These agents are generally colloids, either of the highly hydrated, gel-forming type (gums, gelatine) or else colloidal electrolytes (soaps, sulphonated oils); solid particles are also capable of stabilising emulsions if they also can be adsorbed at the interface. It is generally agreed that the stability of these emulsions is due to the presence of an adsorbed film at the interface, consisting of (*a*) a coherent, mechanically strong gel, (*b*) an orientated unimolecular layer, or (*c*) tightly packed solid particles. Nevertheless many other factors contribute or are alleged to contribute to emulsion stability. Some of the more important of these will now be discussed in connection with the oil and water type of system which has received most study.

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[1] N. V. De Bataafsche Petroleum Maatschappij, Brit. 341,914 (1928).
[2] Lefebvre and Berger, Fr. 723,728 (1930); Brit. 362,299 (1931).
[3] Sparks, U.S. 1,956,779 (1934); McConnaughay, U.S. 1,989,374 (1935).
[4] *J. Hyg.*, **39**, 529 (1939).
[5] *Trans. Faraday Soc.*, **37**, 168 (1941).

The only significant method of measuring stability is one which considers the coalescence of the dispersed droplets of an ageing emulsion or the separation of free internal phase liquid from it. In these systems where oil separation is relatively fast and well defined, mere measurement of its extent after different times will suffice for comparison of stability. More precise data may be obtained by making a size-frequency analysis of an emulsion when freshly prepared and at various times thereafter and plotting specific area of interface against time. King and Mukherjee [1] have applied the size-frequency method with some success and were able to compare emulsions prepared with different agents and under different conditions. Unpublished work by Gilpin shows, however, that the method may give misleading results in certain cases, especially where the concentration of emulsifying agent is small.

As regards stability as affected by the emulsifying agent, qualitative results indicate well enough the differences in stability of emulsions stabilised by agents of diverse character, but for less obvious cases the size-frequency method is alone capable of giving significant results. King's work concerned emulsions stabilised by colloidal electrolyte, hydrophilic colloids and by solids.

The soap-stabilised emulsion is initially very highly dispersed as compared with the other two, but deteriorates relatively quickly, so that, after 30 days it is actually less highly dispersed than the other emulsions. In fact, much the oil originally dispersed had separated as a free layer by this time.

The gelatin-stabilised emulsion, while originally less highly dispersed than the first is much more stable and shows only a gradual decrease in the area of interface. In this system, in distinction to the last, there was no separation of free oil, even after weeks.

A still higher stability characterises the emulsion stabilised by gelatinous alumina in spite of its initial coarseness. Indeed, some emulsions of this type have shown no oil separation during a period of two years and only slight decrease in the specific interface.

It thus appears that emulsion stability is not, in general, a function of the degree of dispersion. If strictly analogous systems alone are discussed, it seems probable that an optimum degree of dispersion exists for maximum stability. Thus with emulsions stabilised by sodium, potassium and ammonium soaps, those emulsions with the highest degree of dispersion (the majority of the droplets were of diameter 0·5–1 μ) are the most stable. With emulsions stabilised by inorganic hydroxides, coarser dispersions are more stable than finer ones.

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[1] King and Mukherjee, *J. Soc. Chem. Ind.*, **58**, 243 (1939); **59**, 185 (1940).

Low interfacial tension, while assisting the dispersion of the internal phase, has no other significance in stability ; its importance lies in its relation to the interfacial adsorption which accompanies it.

EFFECTS OF FREEZING EMULSIONS

Some emulsions are easily broken by freezing, whilst others reconstitute after thawing. The damage is connected with the influence of freezing on the emulsifying agent employed. The concentrated mayonnaise familiar abroad will so break unless the egg yolk is reinforced by a colloid such as pectin. An interesting line of research would be the effect of non-denaturable hydrophilic colloids on the freezing denaturation of proteins.

Newman[1] froze a stable homogeneous emulsion, containing 95 per cent. by volume of benzene in dilute sodium oleate solution. On thawing, the emulsion broke and could not be restored by shaking. The breaking of the emulsion was probably due to the rupture of the soap films around the benzene globules, but the irreversibility was probably only apparent and due to the very slow redissolving in water of the coagulated sodium oleate.

Stability to freezing is important in connection with bitumen emulsions, and patents claim various means of avoiding injury to the emulsion. Hay[2] uses up to 10 per cent. of glycerol or allyl alcohol in the aqueous continuous phase. Roediger[3] employs rosin soap, whilst colophony or coumarone resin is recommended for frost-proof tar emulsions.[4] The incorporation of colloids[5] or volatile organic liquids[6] such as alcohols or acetone is also stated to be effective.

Gabriel[7] has pointed out that the normal soap-stabilised bitumen emulsions used as road dressings are completely coagulated by freezing. He says : " Considerable super-cooling of the emulsions is often possible, but once solidification has taken place, partial or complete coagulation results. The reasons for this behaviour are quite obscure and would form an interesting subject for research. One curious observation should be recorded : if an emulsion of this type is frozen solid and thawed with stirring, to coagulate it, it will be found that the aqueous liquid separating is almost pure water. The emulsifier seems to have completely disappeared and can only be recovered in very small part by continued boiling of the separated bitumen with water. The effect would certainly merit further investigation."

The general problem of the effect of freezing on prepared emulsions remains open to investigation, particularly in relation to the nature of the emulsifying agent employed and the size-frequency analysis of the initial system. The problem of "bound water" may be involved in certain instances.[1]

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[1] *J. Phys. Chem.*, **18**, 45 (1914).

[2] U.S. 1,781,632 (1930).

[3] U.S. 1,988,336 (1935).

[4] Ges. f. Teerstrassenbau m.b.H. Ger. 593,184 (1934).

[5] Nippon Sekiyû K.K., Japan 96,313 (1932).

[6] I. G. Farbenind. A.-G., Brit. 334,426 (1928).

[7] " Technical Aspects of Emulsions " (London, 1935), p. 146.

Vickery[2] has pointed out that theoretically a colloidal system totally free from impurities such as salts and having a continuous phase of water or a pure organic liquid would show no aggregation of the internal phase due to freezing. He has tried mixtures of heptane and carbon tetrachloride (density = 1) emulsified in water with kaolin. "Preliminary experiments with this emulsion have shown that in all probability, critical freezing temperatures and critical salt-concentrations do exist, but so far it has not been possible to eliminate completely the 'rate-of-freezing factor'."

A critical examination of the problem of the measurement of "bound" water by the freezing method has been made by Kistler,[3] who concluded that undercooling of water is at least a partial explanation of the fact that too much water remains unfrozen. He substantiated this idea by experiments on the freezing of W/O emulsions, using toluene and aluminium palmitate (4 per cent.). A colloid mill rendered an emulsion with globules not smaller than 0·2 μ diameter.

Although most of his emulsions were unstable to freezing, breaking and completely freezing at − 20° C., some retained their dispersion and enabled a dilatometer record to be made over some hours. Water-in-kerosene emulsions, stabilised by 2 per cent. of aluminium palmitate, were less stable to freezing.

The emulsion condition precludes any "bound" water due to surface orientation or adsorption. Rather is the result due to the operation of the laws of chance for the appearance of crystal nuclei in minute and isolated globules of water, without the attendant complication of hydrophilic colloid.

FREEZING OF MILK AND CREAM

The most attention to the freezing of emulsions has been devoted to milk and cream for very practical reasons. Unfortunately, these "natural" emulsions are very complex in make-up with proteins and salts present. However, certain interesting results deserve consideration.[4]

Reid[5] deals with the deleterious effect of freezing on several of the physical properties of milk. The first effect of low temperature is the appearance of flakes of Ca caseinate, visible to the eye. Partial destruction of the emulsion takes place, and the natural emulsion is never restored after thawing. The fat content of the upper layers may be three times as high as originally and much higher in the centre portion of the milk than at the periphery. The cream column of the milk decreases as the result of freezing, as the following table by Reid shows.

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[1] Jones and Gortner, *J. Phys. Chem.*, **36**, 387 (1932); Pyenson and Dahle, *J. Dairy Sci.*, **21**, 169; 407; 601 (1938).

[2] *Report of the Food Investigation Board*; year 1928 (London: 1929), p. 24.

[3] *J. Am. Chem. Soc.*, **58**, 901 (1936).

[4] Munkwitz, Berry and Boyer. Univ. Maryland Agr. Expt. Sta., *Bull.*, **344** (1933); Mantovani, *Rev. facultad quim. ind. agr.* (*Univ. nacl. litoral, Argentina*), **3**, 34 (1934); Scheimpflug, *Milchw. Forsch.*, **15**, 183 (1933); Koenig, *Molkerei Ztg.*, **44**, 289 (1930).

[5] Missouri Agr. Expt. Sta., *Research Bull.*, **100** (1927), pp. 14.

TABLE 27

EFFECT OF FREEZING ON THE CREAM LINE OF MILK

Temperature of Freezing °C.	Percentage Loss after Thawing.					
	Frozen 3 hours.			Frozen 5 hours.		
	1 hour.	3 hours.	24 hours.	1 hour.	3 hours.	24 hours.
−17·78	39·00	42·44	45·90	40.75	42·65	45·90
−14·44	38·84	41·82	43·16	40·12	42·47	45·40
−12·22	31·68	33·33	38·34	39·83	41·24	43·40
− 9·44	24·90	29·70	33·20	28·70	33·80	38·88
− 6·67	15·78	24·65	28·67	18·00	26·19	32·70
− 3·89	8·31	13·98	25·57	15·90	27·90	30·10
− 1·11	0·58	4·25	12·19	2·21	5·89	13·04

"The body of the cream of every sample frozen and thawed, when observed after one hour was granular, porous and decidedly coarse. The upper and lower surfaces of the cream columns were irregular and ragged. As time elapsed, these undesirable characteristics gradually disappeared. When the last observations were made after twenty hours the body in almost every sample was described as being quite smooth, free from the marked granular appearance, and the surfaces of the cream column regular and level except in the milk frozen at the extremely low temperatures, in which instances the effect of the freezing remained slightly apparent."

Reid reproduces photomicrographs showing the marked clumping of the butterfat globules in the whole milk frozen at 0° F. (− 17·78° C.), the effect being very pronounced after five hours' freezing.

Highly interesting observations have been made by Webb and Hall,[1] who found that slow freezing of milk or cream caused a gradual precipitation of the caseinate system and an immediate destruction of the emulsion. No change in the heat stability of skim milk due to freezing was detected until the milk had been held frozen for several months at − 18° C. or below; the size of the casein aggregates, therefore, increased very slowly.

The addition of sucrose or raising the solids-not-fat content of cream reduced the destruction of the cream emulsion during slow freezing. For low fat creams, homogenisation slightly retarded fat separation. Freezing destroyed the fat clumps formed in cream by homogenisation and restored to the cream the heat stability which it initially possessed. Table 28 is reproduced from the authors' paper.

"The ability of the homogenisation process to increase protein adsorption and fat clumping in cream was utilised in a method developed to separate some of the milk constituents. It was observed that when homogenised frozen cream was thawed at a temperature below the melting point of the fat, the serum could be drained from the thawing mass, leaving behind a mixture of fat and adsorbed casein. If the melting

[1] *J. Dairy Sci.*, **18**, 275 (1935).

TABLE 28

EFFECT OF HOMOGENISATION UPON FAT SEPARATION IN CREAM DURING FREEZING

(60 minutes at – 18° C.)

Fat in Cream.	Fat Separation * after Thawing.		
	Not homogenised.	Homogenised at 1,500 lbs.	Homogenised at 3,000 lbs.
Per cent.	Per cent.	Per cent.	Per cent.
10	1·4	1·1	0·7
20	7·9	5·7	3·6
30	10·5	16·1	18·5
40	25·6	22·2	24·9

* Fat column readings.

temperature was high enough to liquefy the fat, the material melted as cream and no separation was possible. The fat-casein mixture could be washed with ice-water without loss to remove traces of serum." The mixture could be used to prepare normal casein or to raise the protein solids of ice-cream mix.

An examination of the freezing and thawing of milk homogenised at various pressures has just been reported by Trout.[1] Milk was homogenised at 0, 500, 1,500, 2,500 and 3,500 lbs. per square inch pressure, bottled and tempered at 40° F. for 24 hours and then exposed to 0° F. for three hours. Then a ½-inch hole was drilled in the frozen plug, through which the unfrozen portion was poured.

It was found that a slightly greater percentage of homogenised than unhomogenised milk froze in a given period at 0° F. When creaming was inhibited by homogenisation the unfrozen portion was relatively richer in fat and solids-not-fat than the frozen portion. When creaming occurred, as in the homogenised milk, the frozen portion was richer in fat but lower in solids-not-fat than the unfrozen portion. Frozen homogenised milk upon thawing exhibited no flakiness which was commonly noted when unhomogenised milk was frozen and thawed, but did exhibit a watery appearance at the surface layers which was more pronounced when the frozen milk was thawed slowly. When milk, heated to inhibit creaming, was frozen and thawed, the fat tended to rise to form a cream layer, in contrast to the movement of fat in the thawed frozen homogenised milk.

Baldwin and Doan[2] have made detailed studies on the freezing of milk and cream. Their first paper deals with the effect of fat concentration upon the distribution of constituents in the frozen and unfrozen portions of partially frozen milk and cream. They state that when whole milk is partially frozen in an undisturbed state, the fat concentration in the frozen and unfrozen portions over the entire range of freezing is dependent upon the cream rising phenomenon of the milk and its speed relative to the speed of freezing and also to some extent upon the size and shape of the container. Increasing fat concentrations in milk or cream retard the diffusion of the milk constituents (colloidal and soluble) into the unfrozen portion of the freezing products, and when the fat concentration reaches 25 per cent., such diffusion is practically prevented and the cream freezes homogeneously. The diffusion is possibly inhibited because of the increased viscosity with increasing fat content and also because of the more effective sealing of the interstices between the developing ice crystals by the increased amount of fat in the form of solidified fat globules.

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[1] *J. Dairy Sci.*, **24**, 277 (1941).

[2] *Ibid.*, **18**, 629 (1935); **19**, 225 (1936).

Their second deals with the destruction of the fat emulsion in frozen cream.[1] Commercially pasteurised cream containing 25 and 40 per cent. fat and 40 per cent. fat + 10 per cent. sucrose, respectively, were frozen in 2-quart tin containers, without agitation, in still air, at −23° to − 28° C. until congealed to varying degrees, approximately 9–10 hours being required to freeze to apparent solidity. After freezing the samples were thawed in a water bath at 10° C., stirred when all the ice was melted, and the whole poured on a 30-mesh screen. The material on the screen was analysed for fat.

There was marked de-emulsification as the fat content of the initial cream was greater. The beneficial influence of sugar was very evident. "Apparently the fat emulsion was not affected appreciably until freezing had progressed to the point where 50 per cent. of the 40 per cent. cream was congealed, 80 per cent. of the 25 per cent. cream was frozen and until the 40 per cent. cream containing sucrose was practically frozen solid. In all three products, however, the rate of freezing was most marked when the point of solidity was approached or attained. When the creams were frozen to apparent solidity, the 40 per cent. cream had, on the average, over 80 per cent. of the fat thrown out of emulsion, the 25 per cent. cream about 30 per cent., and the 40 per cent. cream with sucrose about 15 per cent."

Special attention was given to the pressure developed in freezing cream, due to the early congelation of the surface of the milk which tended to restrict further expansion by ice in the unfrozen centre. Indeed, the authors conclude " that in the destruction of the fat emulsion brought about by the unagitated freezing of cream, the pressure developed by the congealing water is causative factor of most importance." Their argument however, is far from convincing in view of their added or collateral argument : " actually pressure may be an important factor in the destruction of the fat emulsion of milk or cream by whatever means accomplished. In the churning of cream, the tremendous concussion and agitation undoubtedly cause localised, intermittent zones of pressure and the rapidly moving layers of cream, very likely, cause pressure of fat globule on fat globule, gradually wearing away or rupturing the layer of adsorbed protective covering and allowing the free fat to coalesce or adhere to other free fat in such a manner that butter aggregates are gradually built up in which the individual globules eventually lose their identity." This, an old idea, is not the explanation of churning (see p. 432), whilst the further conclusion that "the stability of the protein as an emulsifying or protective colloid is not an important factor within the limits of its variability under commercial conditions," must certainly be questioned.

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[1] A review, with sixty-nine references, has recently been presented on frozen cream by Dahle, *J. Dairy Sci.*, **24**, 245 (1941).

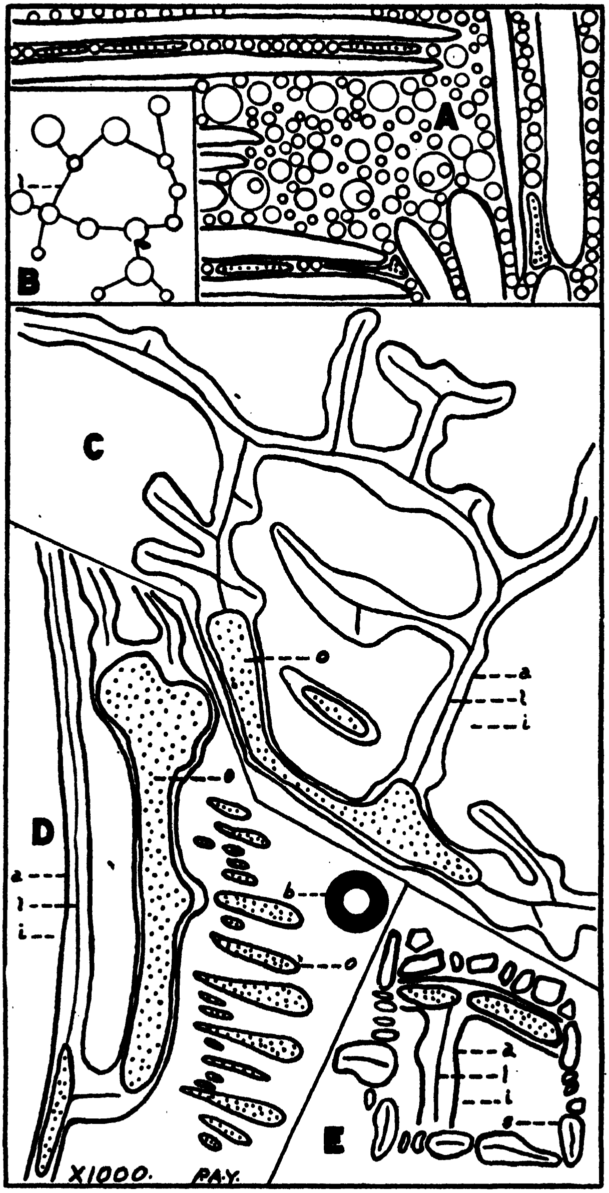

FIG. 30. Diagrammatic drawing showing common arrangements of ice, oil, gas and aqueous solution of gas, soaps, and cresols in cresoap emulsions of 2 and 4 per cent. oils frozen on microscope slides. Stippled areas represent irregular masses of oil deformed by ice crystals. In parts B to E, the lines *l* represent the blue lines of gas and liquid between nearly touching ice crystals (Young).

Young [1] has investigated freezing phenomena in cresoap emulsions of petroleum oils and has made highly important observations, in some cases staining the oil with oil red O. The stock of cresoap-miscible oils was made by dissolving 5·5 per cent. of potassium fish-oil soap and 4·5 per cent. of cresols in the mineral oils. The emulsions were frozen in test tubes and on microscope slides, melting being induced by holding hot needles near them.

The results of freezing on microscope slides as observed under magnifications of 50 to 600 times revealed the following sequence of phenomena in the cresoap emulsions of 2 and 4 per cent. mineral oils. (See Fig. 30 reproduced from Young's report).

(1) The emulsion field was rapidly invaded by long needles of ice, which crowded the oil globules into narrowing channels between the ice crystals; many globules were so contacted that they coalesced to form elongated masses of oil (Fig. 30A). The oil globules and masses occurred in straight rows as long as 1·7 mm. Evolution of gas took place while ice crystals formed in the freezing emulsions (Fig. 30D).

(2) Spaces containing gas or aqueous solutions appeared as blue lines nearly 0·2 μ wide between adjacent ice crystals (Fig. 30B). Refraction of the light by the lens was responsible for the blue tint. The colder bottoms of the slides caused the first formation of horizontal lamellæ of ice.

(3) New horizontal lamellæ of ice formed on this bottom layer until all the available water was crystallised. Many of these super-imposed crystals were separated by wide channels of gas, and by channels of aqueous solution of gas, cresols and soaps surrounding masses of oil (Fig. 30C, D, E). These channels were compressed between the ice crystals and lay above many of the blue lines.

(4) Melting of the frozen emulsions caused widening channels of clear water to replace the blue lines. The elongated bodies of oil and gas suddenly became circular in outline. Solution of many gas bubbles in the water was noted.

(5) Oil globules moved rapidly and dispersed in the widening channels of water between melting crystals of ice. Many of the large masses of oils partly or entirely re-emulsified in the water liberated from the ice. Freezing and melting apparently increased slightly the predominating sizes of the oil globules.

Young mentions that the channels of oil, aqueous solution and gas between ice crystals were straighter and less numerous in the frozen emulsions of 2 per cent. oil than in those of 4 per cent. oil. Many masses of oil were not enclosed in the channels between ice crystals (Fig. 30D).

The sequence of the freezing phenomena when emulsions were frozen in test tubes is illustrated by Fig. 31 given by Young.

(1) Near the glass, layers of transparent ice 1 to 7 mm. thick formed, concentrating the oil globules, gas bubbles and aqueous solution near the centres of the tubes (Fig. 31F). Part of the outer transparent ice commonly contained long, parallel, or radial pockets of gas.

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[1] *Plant Physiology*, 9, 795 (1934).

(2) Needles (Fig. 31A), lamellæ (Fig. 31D, E), and polyhedrons (Fig. 31A, C) of ice formed in the emulsions, concentrating the oil globules, gas bubbles and aqueous solution between these compound ice crystals.

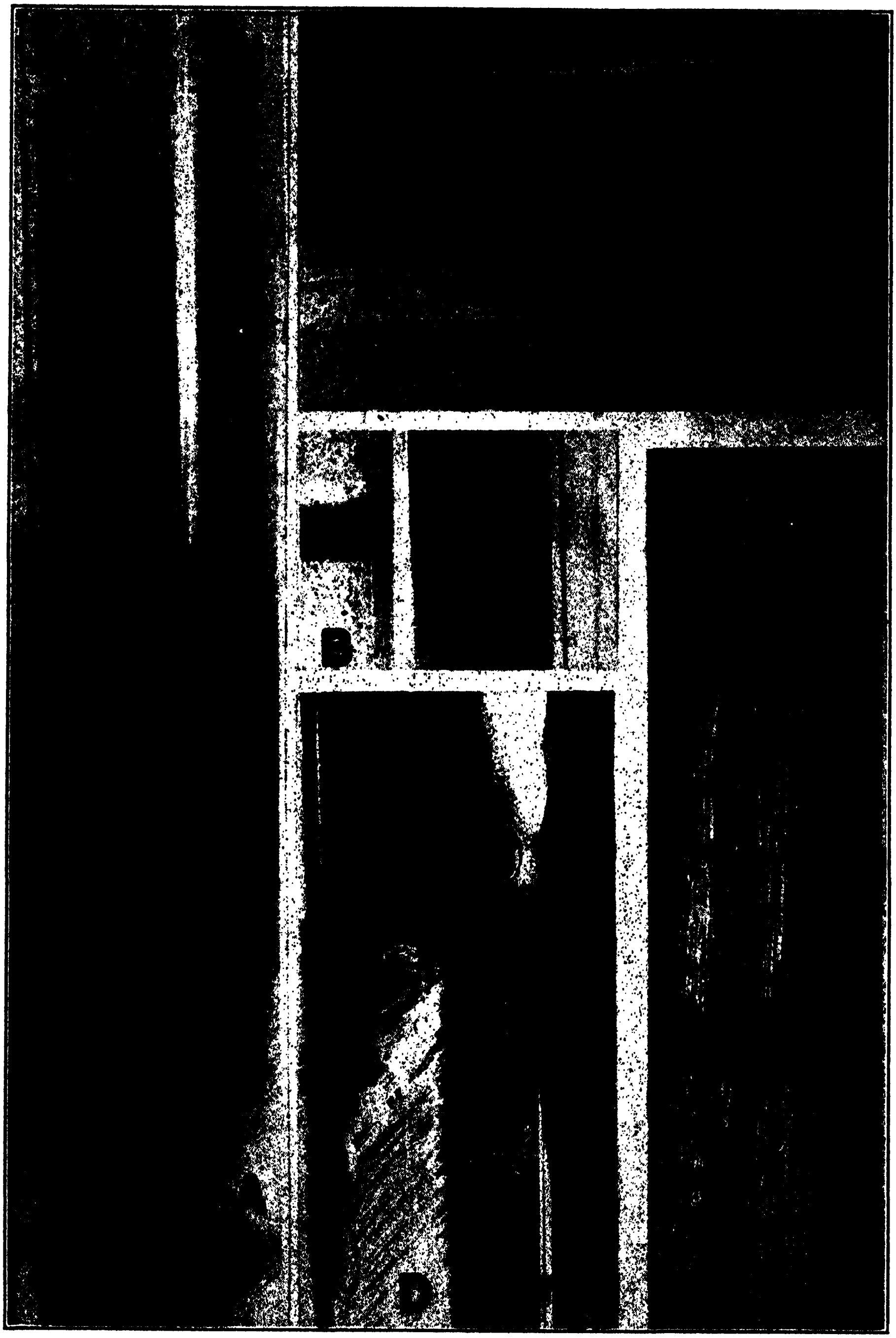

FIG. 31. Emulsions frozen in test tubes (Young).

(3) As freezing proceeded, the ice crystals enlarged (removing water

from the channels) until the milky-ice columns became translucent and lost their milkiness, apparently because the lamellæ and polyhedrons of ice held masses of oils, gas, and concentrated aqueous solution of gas, soaps, and cresols in such narrow layers and channels between them (Fig. 30C, D, E).

(4) One to four horizontal cracks developed in most of the expanding columns of freezing emulsions (Fig. 30A, B, E, F). By the use of coloured oil it was observed that the cracks contained less oil than the other parts of the ice columns.

As regards melting frozen emulsions, the finest visible evidence of melting was the formation of milky emulsions (Fig. 30D). It was found that the oil globules 0·1 to 20μ diameter usually became redispersed in water liberated from the ice, whilst many of the larger masses of oil were in part redispersed; convection currents in water melting from ice no doubt assisted dispersion.

Under the title: "Breaking Emulsions by Freezing," Rochow and Mason[1] have presented a detailed and very interesting account of experimental work. They summarise their conclusions that breaking by freezing may be ascribed to the following causes in sequence:—

(1) Withdrawal of free and/or bound water from the films between touching globules, by crystallisation as ice, or by concentrating solutes present.

(2) Establishment of true contact between adjacent films of emulsifier, with loss of the orienting influence of water.

(3) Diffusion of the emulsifier in the film away from these thick regions.

(4) Decrease in film area and coalescence of globules as soon as thawing of the ice permits them to change shape.

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[1] *Ind. Eng. Chem.*, **28**, 1296 (1936).

CHAPTER VI

THEORIES OF EMULSIONS

ALTHOUGH in three-phase emulsions it has long been recognised that adsorbed material at the liquid/liquid interface usually forms a stabilising film around the dispersed globules, emphasis has from time to time been laid on other factors as responsible not only for the incidence but the stability of the systems. Any satisfactory theory of emulsions must take into account the phenomena of dual emulsions and the inversion of phases, the now very wide range of emulsifying agents of extreme diversity and, sooner or later, the peculiar effects of certain mechanical treatments such as the experiments described by Cheesman and King [1] and Clayton.[2]

One of the outstanding difficulties has been the absence of some well-defined criterion by which to measure emulsion stability, since the grain-size alone is not sufficient guide. Whilst commercial homogenisation is extraordinarily effective in stabilising emulsions, there are many laboratory results pointing to very stable emulsions where the grain-size is much coarser than exhibited in commercial emulsions.

It is natural that earlier workers such as Hillyer,[3] Marshall,[4] White and Marden,[5] Holmes and Child,[6] and Canals and Mousseron [7] have stressed the importance of viscosity in emulsion stability; it is to-day quite clear that viscosity is not the cause of emulsion *formation*. Viscosity is an aid to emulsification solely by virtue of the hindrance offered to coalescence of the dispersed globules. King [8] has stated, and the present writer agrees, that the viscosity of an emulsion is a function, not only of the phase ratio volumetrically, but of the nature and condition of the emulsifying agent. Further, the viscosity of the dispersed liquid can usually be neglected as a factor influencing the viscosity of the finished emulsion.

Where the emulsifying agent is a hydrophilic colloid the viscosity factor may assume importance, according to the extent of hydration prevailing. This is really the only sound basis for the old *hydration theory* due to Fischer [9] who postulated that oil cannot be emulsified in a hydrated colloid until a certain minimum amount of water is present and, conversely, instability follows if too much water is present.

THE SURFACE TENSION THEORY OF EMULSIONS

Quincke [10] prepared emulsions of various oils in solutions of NaOH or gum arabic, and showed that the interfacial tensions between the oils and these solutions were lower than those between the oils and pure water. Previous works by Brücke[1] and Gad[2] had shown that rancid oils, or oils containing free fatty acids, gave better emulsions in dilute solutions of borax or sodium carbonate than did purer oils. Gad even claimed that drops of oil containing free fatty acid gave spontaneous emulsions in 0·25 per cent. aqueous sodium carbonate. Spontaneous emulsions have also been obtained by Bhatnagar.[3] Quincke, commenting on the work of Gad, Brücke and himself, suggested that the ease of emulsification varied with the acidity and viscosity of the oil, the concentration of the alkaline solution, and the solubility in water of the resulting soap.

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[1] *Trans. Faraday Soc.*, **34**, 594 (1938).
[2] *Margarine J.*, **2**, 503 (1920); *Kolloid-Z.*, **28**, 204 (1920).
[3] *J. Am. Chem. Soc.*, **25**, 513 (1903).
[4] *Pharm. J.*, **28**, 264 (1909).
[5] *J. Phys. Chem.*, **24**, 629 (1920).
[6] *J. Am. Chem. Soc.*, **42**, 2049 (1920).
[7] *Bull. sci. pharmacol.*, **33**, 283 (1926).
[8] *Trans. Faraday Soc.*, **37**, 168 (1941).
[9] Fischer and Hooker, "Fats and Fatty Degeneration" (N.Y., 1917), p. 5.
[10] *Wied. Ann.*, **35**, 589 (1888).

Later, Donnan[4] investigated the interfacial tensions between oils and alkaline solutions, using the drop-pipette,[5] by means of which he determined the number of drops of oil rising through the alkaline solution under standard conditions. The number of drops is, as a first approximation, directly proportional to the ease of emulsification of the oil in the alkaline solution. At a concentration of NaOH of 0·0013 gram.-mols./litre, the oil streamed through the aqueous phase and the drop-number was impossible to estimate. Evidently, increasing the amount of NaOH in the aqueous phase causes a lowering of the interfacial tension. This lowering was shown by Donnan to be due to the formation of soap, since a carefully purified neutral oil gave the same drop-number in NaOH as in water.[6] Thus :—

Oil.	Reaction.	Drop-Number in Water.	Drop-Number in N/1000 NaOH.
Commercial olive oil .	Acid.	58	331
Purified olive oil . .	Neutral.	58	58

In order to prove that soap was not formed by a surface saponification of glyceride, Donnan employed a paraffin hydrocarbon oil. Thus :—

Oil.	Acidity.	Drop-Number.	
		Water.	N/1000 NaOH.
Hydrocarbon	Neutral	47	52·7
Hydrocarbon	0·6 per cent. commercial stearic acid added . .	48·5	320·0

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[1] *Sitzungsber. Akad. Wiss. Wien.*, **61** (II.), 362 (1870).

[2] E. du Bois Reymond, *Arch. Anat. Phys.* (1878), 181.

[3] Private communication to the author. Cf. also Maday, *Zentr. Physiol.*, **27**, 381 (1914)

[4] *Z. physik. Chem.*, **31**, 42 (1899).

[5] See p. 460.

[6] *Vide* Rachford (*J. Physiol.*, **12**, 72 (1891)), who found that a pure neutral oil could not be emulsified in dilute sodium carbonate solution. On the other hand, Hartridge and Peters (*Proc. Roy. Soc.*, **A**, **101**, 362 (1922)) repeated Donnan's experiment, and concluded " we must admit the failure of all our attempts to prepare an (olive) oil which did not give a fall in interfacial tension when N/1000 NaOH was substituted for distilled water."

Donnan now investigated the dispersion in NaOH of hydrocarbon oils containing different members of the fatty acid series, and found that the interfacial tension diminution was peculiar to the higher fatty acids, from lauric acid onwards. Drop-numbers of hydrocarbon oils containing 0·7 per cent. free fatty acid had the following values :—

Acid.	Drop-Number in Water.	Drop-Number in N/1000 NaOH.
(C_1) Formic . . .	34	37
(C_2) Acetic . . .	38	38
(C_4) Butyric . . .	38	35
(C_8) Caprylic . . .	44	47
(C_{12}) Lauric . . .	43	82

Having suggested that emulsification was intimately connected with the formation of a layer of soap solution at the oil-water interface, Donnan [1] investigated the relation between the concentrations of solutions of the sodium salts of the various fatty acids and the interfacial tension between these solutions and a high-grade hydrocarbon oil containing only 0·1 per cent. free fatty acid. The interfacial tensions were again measured by the drop-pipette and calculated on the basis that the interfacial tension between the oil and water = 1.

The results are expressed graphically in Figs. 32 and 33. The ordinates in Fig. 32 are the relative interfacial tensions, the abscissæ being concentrations of the sodium salts. Fig. 33 expresses the relation between the relative interfacial tensions and the molecular weights of the fatty acids concerned. Sodium caprylate (C_8) is the first to show a marked effect in lowering the interfacial tension, the effect then increasing rapidly with rise in the molecular weight.

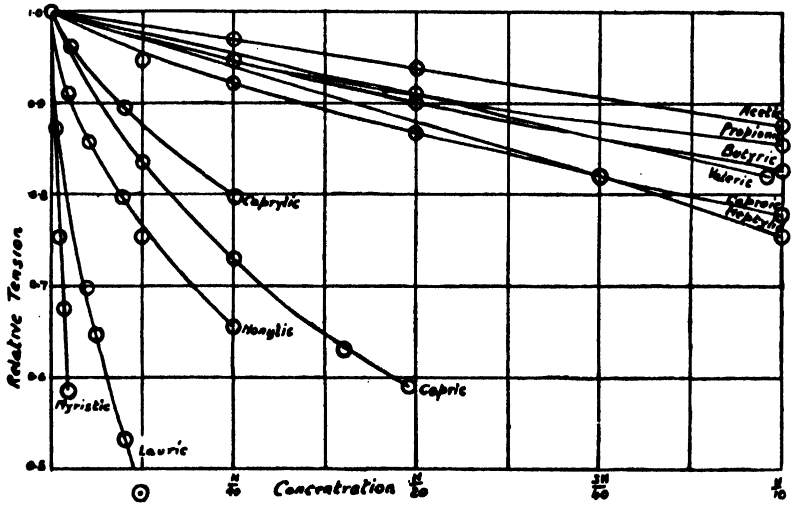

FIG. 32.

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[1] *Kolloid-Z.*, 4, 208 (1910).

Donnan and Potts concluded that the sodium salts of the higher fatty acids were adsorbed (following Gibbs' rule) at the separating boundary between the oil and solution. This is the basis of the modern theory of emulsions.

It was pointed out that Mayer, Schaeffer and Terroine [1] found, by an ultramicroscope examination of the sodium salts of the fatty acids, that the lower members gave ordinary aqueous solutions, whilst the solutions of sodium heptylate, caprylate and laurate were colloidal. The characteristics of soap solution first appear in the series with sodium caprylate, becoming very pronounced with sodium laurate.

Donnan and Potts now investigated the emulsifying power of the various sodium salts with respect to a pure hydrocarbon oil. The sodium salts of the lower fatty acids gave no emulsions, sodium caprate and nonylate gave dilute emulsions, whilst sodium laurate and myristate promoted fairly satisfactory emulsification. For each salt capable of promoting emulsification there appeared an optimum concentration where the emulsifying power was a maximum. There seems to be a salting-out action, possibly due to the positive sodium ions coagulating the negatively-charged oil drops. Evidently, up to sodium laurate, ineffective emulsifying properties are exhibited because the coagulating action of the sodium ions exceeds the effect of the emulsifying tendency due to interfacial tension lowering.

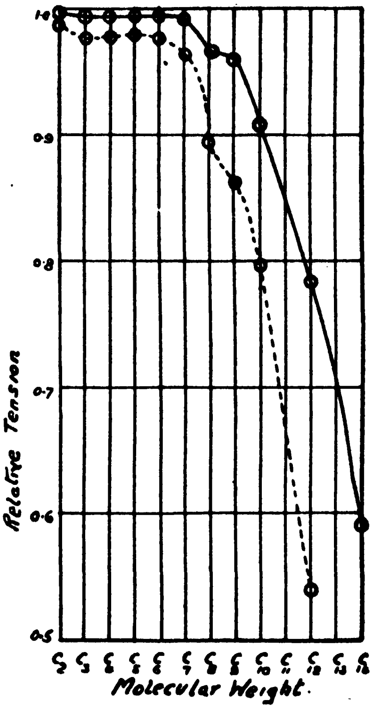

FIG. 33.

These results have been confirmed by Dubrisay and Picard,[2] and by Lascaray.[3] The latter investigated the surface tensions of solutions of the pure sodium salts of the acids in the fatty acid series, using the Traube stalagmometer. The surface tension changes in regular fashion from the surface inactive sodium formate up to the higher members of the series exhibiting marked surface activity. The surface activity regularly rises and reaches a maximum with sodium myristate, thereafter falling, until the higher members (sodium cerotate, $NaC_{26}H_5O$) show no surface activity. Lascaray also observed that the "soap properties" of a solution are not only connected with the molecular weight of the soap, but also with the concentration of the solution.

As a result of their work, Donnan and Potts concluded that "changes in the interfacial tension at the boundary oil/water are connected with changes in electrical potential, in which the selective adsorption of ions probably plays a part." They further concluded that emulsified globules of oil were surrounded by a "very viscous or possibly gelatinous film which offers resistance to the coalescence of the globules." Indications of such film formation around oil globules emulsified in solutions of bile salts were obtained by Lewis.[1] This film is the result of adsorption consequent upon the lowering of the interfacial tension at the boundary oil/water. A somewhat similar conclusion has also been reached by Hillyer,[2] who recognised that emulsification was intimately connected with "a small surface tension between oil and the emulsifying agent." He did not, however, realise the fundamental nature of the facts involved and their relation to the Gibbs' rule. Later work in Donnan's laboratory by Lewis, Ellis, Powis and Barker amplified and extended the surface tension theory, and correlated it with adsorption, electrical charges and the coagulation of emulsions.

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[1] *Comptes rend.*, **146**, 484 (1908).

[2] *Chimie et industrie*, Special No. (May, 1924), 121; *Bull. soc. chim.* (1925), 996; *Compt. rend.*, **178**, 205, 1976 (1924).

[3] *Kolloid-Z.*, **34**, 73 (1924).

Ramsden [3] arrived at conclusions very similar to those of Donnan by an entirely different avenue. He demonstrated that many colloidal solutions and suspensions could be coagulated by mere agitation, forming fibrous or gelatinous membranes of an irreversible character. Regarding emulsions, Ramsden believed that one of the most important factors involved was the presence of a highly viscous gelatinous film enveloping the oil globules, this film being the result of adsorption, accompanied by a diminution of surface energy at the oil/water interface.

The interfacial tension of liquid fatty acids and their solutions in benzene against aqueous buffer solutions of varying *p*H values has been determined by Peters and Hartridge.[4] On the acid side, from *p*H 3 to 5, the interfacial tension remains constant, at higher *p*H values falls slowly, but on the alkaline side rapidly diminishes. At *p*H $>$ 8 the interfacial tension is very low indeed, owing to the formation of soap at the interface. As expected, it was found that when a pure glyceride like olein makes an interface with different buffered solutions, but of the same *p*H value, the interfacial tension is the same. Another conclusion experimentally established was that change of interfacial tension with change of *p*H value is only shown by those substances containing the chemically reactive ionisable group —COOH, free or in combination with glycerol.

Peters [5] extended the investigation, determining the interfacial tension between benzene solutions of long chain carbon compounds and aqueous solutions of varying *p*H value. He showed that with solutions of pure, long chain fatty acids dissolved in benzene the decrease in interfacial tension sets in at *p*H 5·5 approximately and extends to *p*H 9·5 approximately, with a reverse change occurring in the case of a long chain amine, hexadecylamine. Peters accepts the view that the changes in interfacial tension depend on changes which occur in a monomolecular

[1] *Phil. Mag.* (April, 1908), p. 499.

[2] *J. Am. Chem. Soc.*, **25**, 513 (1903). But see the peculiar results with mercury/water "emulsions" recorded by Sivertz, Naylor and Tartar, *ibid.*, **58**, 782 (1936).

[3] See p. 18.

[4] *Proc. Roy. Soc.*, **A**, **101**, 348 (1922). See also Gay and Donnet, *J. chim. physique*, **29**, 385 (1932).

[5] *Ibid.*, **A**, **133**, 140 (1931).

layer at the liquid/liquid boundary, and that there is no simple relation between the decrease in interfacial tension and the degree of interfacial ionisation. He inclines to the opinion "that there is a state of the polar groups at the interface possibly connected with adsorption of ions at a polarised layer of water molecules which precedes that of true ionisation and is reflected in the changes observed."

ADSORBED FILM THEORY OF EMULSIONS

We have seen that emulsions of oil in water or of water in oil may be prepared by suitably choosing the emulsifying agent, which is invariably necessary in order to obtain emulsions of even moderate concentration of the dispersed phase. Such emulsions may also be inverted to systems of the opposite type by adding suitable electrolytes. Any general theory of emulsions and their stability must be capable of including and explaining all the above facts. The present widely-accepted theory of emulsions, postulating an adsorbed film or membrane around the dispersed globules, has been developed from Donnan's earlier work on the interfacial tension in emulsions.

Bancroft,[1] in 1913, deduced the underlying principles of the modern theory. He accepted Donnan's surface tension theory, but pointed out its limitations, the chief of which was that Donnan only formulated the conditions for the formation and stability of oil-in-water emulsions; *two* emulsion types were not considered. Donnan's idea that, in the case of soap emulsions, the gelatinous soap film around the oil globules is part of the water phase, but differing in concentration, was replaced by considering this film as a *separate* phase separating the oil and water phases. On the relative magnitudes of the surface tensions on each side of this film depend the type of emulsion promoted. Both the oil and the water phase are considered to wet the film and to be adsorbed by it, so that, in general, there will exist a difference in the surface tensions on the two sides. Due to this difference, the film will bend, the side with the higher surface tension becomes concave, consequently tending to envelop liquid on that side. Thus, theoretically, a liquid O will be dispersed as drops in a liquid W when the interfacial tension between W and the film is less than the interfacial tension between O and the film.

On the nature of the emulsifying agent depends the type of emulsion produced. The coherency and permanency of the film formed are determining factors in the stability of the emulsion. As a corollary to this, Bancroft formulated that "a hydrophile colloid will tend to make water the dispersing phase, while a hydrophobe colloid will tend to make water the dispersed phase."

In a later paper Bancroft [2] extended his theory and pointed out that, for a substance to act as an emulsifying agent, it must necessarily be adsorbed into the surface separating the two liquids and form a coherent film there. If it was not so adsorbed into the dineric interface it would be unable to form a film enveloping globules of one of the liquids.

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[1] *J. Phys. Chem.*, **17**, 514 (1913). See Hildebrand, *ibid.*, **45**, 1303 (1941).

[2] *Ibid.*, **19**, 275 (1915).

The idea that a film has two surfaces and accordingly will have two surface tensions if in contact with the different phases has been further developed by Bancroft and Tucker,[1] who state that Gibbs gave a diagram in which it is recognised that these two surface tensions are not necessarily equal. The film will tend to curve towards the side having the higher surface tension ; the dispersed liquid is on the side of the film having the higher surface tension.

An experimental technique was devised, whereby the behaviour of a drop of liquid placed on the surface of a second immiscible liquid was followed visually. The criterion was that the flattening of a drop indicates a decreased surface tension ; conversely, a spherical contour indicates increased surface tension. The following summarises the author's results.

TABLE 29

VISUAL BEHAVIOUR OF DROPS OF LIQUID SURFACES

Bulk Liquid.	Drop.	Behaviour.
Aqueous Na oleate	Benzene	Nearly spherical drop somewhat immersed in the soap solution. Addition of lime-water caused the drop to spread as a film on the aqueous surface.
Aqueous Ca oleate	Benzene	Spreads as a film.
Benzene	Aqueous Na oleate	Film forms underneath benzene. Addition of aqueous Ca oleate leads to a convex drop beneath the benzene and this drop does not readily coalesce with another.
Aqueous Na oleate	Olive oil	Drop stands up on the surface.
Aqueous Ca oleate	Olive oil	Spreads as a thin film.
Olive oil	Aqueous Na oleate	Spreads as a thin film.
Olive oil	Aqueous Ca oleate.	Drop stands up on the surface.

Clowes [2] has submitted Bancroft's ideas to experimental investigation, and has published important work on emulsion reversals which makes possible a fairly definite formulation of the theory of emulsion type and stability. At the outset he pointed out that the production of even a temporary emulsion with more than a very small disperse-phase concentration appears to depend on the presence in the system of a third substance which can be adsorbed at the dineric interface and form a protecting film around the dispersed globules, oil or water, as the case may be.[3] The dispersing and the stabilising effects of this film may be due in various measures to (*a*) the lowering of the interfacial tension between the two phases, tending to oppose coalescence of the globules ;

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[1] *Ibid.*, **31**, 1681 (1927). See Chang, *Trans. Science Soc. China*, **7**, 17 (1931).
[2] *J. Phys. Chem.*, **20**, 407 (1916).
[3] Cf. Holmes and Cameron, *J. Am. Chem. Soc.*, **44**, 70 (1922).

(*b*) the conferring of an electric charge on the dispersed phase, electrical repulsion opposing coalescence ; (*c*) a mechanical action aiding in keeping the particles apart. Such films have been visualised by Clowes and other workers.

Clowes re-worded Bancroft's theory concerning this film formation and the type of emulsion produced. Considering the system oil and soap solution : "The soaps tend to concentrate at the interface between oil and water and to form a coherent film. Soaps of monovalent cations, being readily dispersed in water, but not in oil, form a film or diaphragm which is wetted more readily by water than by oil ; consequently the surface tension is lower on the water side than on the oil side. Since the area of the inside face of a film surrounding a sphere is smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. On the other hand, a film composed of soaps of di- or trivalent cations, being freely dispersed in oil, but not in water, is wetted more readily by the oil than by the water. The surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase." This is schematically represented by Clowes as in Fig. 34.

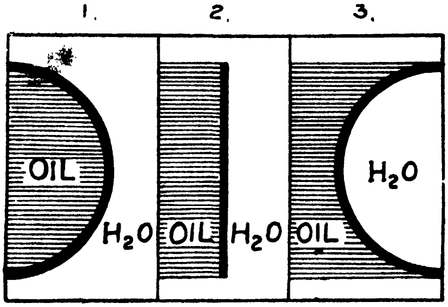

FIG. 34. The two types of emulsions (Clowes).

When opposing emulsifying agents are present in the system to an extent that their effects are counterbalancing, the film does not curve in either direction, so that, when agitation ceases, the two phases readily settle out under gravitational influence. In other words, the surface tension on each side of the film is the same.

Bhatnagar[1] has brought the adsorption film theory to an even more definite form than Clowes, laying more stress than previous workers on the *wetting* of the adsorbed film, a factor also clear to Pickering in his experiments with solid emulsifying agents.

On this theory there are no limiting concentrations of oil in water or *vice versâ*, dispersion being independent of the volumes employed. Emphasis is rather laid on the fact that emulsification is influenced by (1) the mass of the emulsifying agent present, (2) the ease with which this agent can be adsorbed at the interfacial separating surface, (3) the nature of the ions adsorbed by the resultant film.

Bhatnagar[2] has made a generalisation on emulsion systems : "All emulsifying agents having an excess of negative ions on them and wetted by water will yield oil-in-water emulsions, while those having an excess of adsorbed positive ions and wetted by oil will give water-in-oil emulsions."

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[1] *J. Chem. Soc.*, **120**, 1768 (1921).
[2] *Loc. cit.*

He emphasises that the two main factors governing the process of emulsification are (*a*) the relative wetting power of the two phases with respect to the emulsifying agent,[1] and (*b*) the surface potential of the membrane between the phases. Reversal of phases is considered as being due to changes in this membrane with respect to either or both of these factors.

THE ORIENTED WEDGE THEORY

The interfacial tension between water and benzene and the influence thereon of sodium and magnesium oleates have been investigated in some detail by Harkins, Davies and Clark.[2] Their results lead them to the conclusion that the *type* of emulsion produced is intimately connected with the *number of oleate radicals* in the molecule of the soap used. On the packing and orientation of the emulsifier (soap) at the dineric interface depends the type of emulsion promoted. The sign and magnitude of the electromagnetic field at the surface of the emulsion globules are also considered to be dependent on the molecular orientation at the interface.

The underlying idea is that for the dispersed globules to be stable the adsorbed molecules (together with adsorbed ions) in the interface must fit the curvature of the drop. For very small drops " the setting and the shape of the molecules become of extreme importance in determining both the surface energy and the other electromagnetic energy relations." The condition for stable emulsions is a zero free-surface energy at the interface drop/continuous phase. This corresponds to the miscibility of two pure liquids whose interfacial tension is very low.

The molecular orientation theory has not only to account for the orientation of solutes at the dineric interface, but has also to deal with the adsorption of finely-divided solids, since numerous instances are known where such solids promote emulsions of the oil-in-water or the water-in-oil type. From Langmuir's work on the adsorption of liquid by a solid it seems likely that the molecules of liquid are orientated, and they pack into the surface layer of a solid, comparable to the packing of oil films on water. Langmuir postulates that " in general there will be a *tendency* for the number of molecules adsorbed to bear a simple integral relation to the number of atoms exposed in the surface of the solid. The configurations of the adsorbed molecules in general are of great influence in determining the number of molecules that can be adsorbed per unit area."

The extension of this theory to solid emulsifiers is that the type of emulsion produced when a finely-divided solid and two immiscible liquids are emulsified together will depend on the molecular orientation of the liquids at the solid/liquid interface. This is, of course, directly connected with the nature of the intermolecular attractions of the solid and liquids. Such attraction we recognise in peptisation and in wetting. The question of the preferential wetting of the solid now arises, leading to the conclusion that the important factor involved is the angle between the liquid/liquid interface and the solid/liquid interface for the liquid—dispersed or continuous phase—in question.

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[1] Cf. Seelich, *Fette u. Seifen*, **46**, 139 (1939).

[2] *J. Am. Chem. Soc.*, **39**, 586 (1917).

The idea advanced by Harkins, Davies and Clark[1] that the curvature of the interfacial film is determined by the orientation of the molecules in the interface has led to several investigations. Finkle, Draper and Hildebrand,[2] using soaps as emulsifiers, correlated the curvature of the film of emulsifier with the atomic diameters of the metals. Consider water and a liquid of low polarity like benzene. Any soap will be adsorbed at the interface to form a film which will become convex on the water side, provided the polar group, in the water, occupies more space than is necessary for the closest packing of the hydrocarbon chain. The direction and degree of curvature should vary with (*a*) the volume of the metal, being more convex the larger this volume; (*b*) the valence, *i.e.*, the number of hydrocarbon chains attached to a single metallic atom. Where the cross-section of the hydrocarbon chain and the metallic end are of the same magnitude, there will be no tendency to curvature and no very stable emulsion, in spite of the high adsorption at the interface which is still possible. Thus theory demands, and the authors found, that the ability of soaps of Cs, K, Na, Ag, to emulsify oil in water should decrease in this order, and that the ability of soaps of Ca, Mg, Zn, Al, Fe, to emulsify water in oil should increase in this order.

This "Oriented Wedge Theory" was apparently supported by the work of Harkins and Keith.[3] It was then investigated in more detail by Harkins and Beeman.[4] Grain-size analyses of emulsions were made, but the "results give no proof for or against the oriented wedge theory; they only indicate that some of the evidence which seemed to support it is not valid."

Later experiments by the same authors[5] brought them to the conclusion: "There is another more proper point of view according to which the oriented wedge theory does not indicate any such decrease in size of the droplets in the change from sodium to caesium. The negative oleate ions are adsorbed at the oil/water interface with the hydrocarbon radical toward the oil and the $-COO^-$ group toward the water. The Na^+ or Cs^+ ions are held to these by electrostatic attractions alone, so the alkali ions form a diffuse but extremely thin positively charged layer, in which the distribution may follow the Boltzmann *e*-theorem. A part of the soap in the film is present as oleic acid formed by hydrolysis. From this point of view it seems improbable that the sizes of the atoms will produce any marked influence upon the sizes of the droplets. It is known, too, that the smaller the alkali atom, the more highly hydrated is its ion. When, on the other hand, the ion of the metal is bi- or tri-valent, the electrostatic relations are such that in general two $RCCO^-$ ions are held by only one M^{++} ion. Such conditions are favourable to the expansion of that side of the film which is turned toward the oil by the spreading of the hydrocarbon chains. Thus the addition of aluminium nitrate to an emulsion produced by sodium oleate inverts the emulsion and changes it to the water-in-oil type."

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[1] *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).

[2] *Ibid.*, **45**, 2780 (1923).

[3] *Science*, **59**, 463 (1924).

[4] *Proc. Nat. Acad. Sci.*, **11**, 631 (1925).

[5] *J. Am. Chem. Soc.*, **51**, 1674 (1929).

The investigation of Wellman and Tartar[1] "emphatically contradicts the oriented wedge theory of emulsions." The adsorbed phase or *third phase*, responsible for emulsion stability, is in no way dependent on the relative diameters of the two ends of the soap molecule.

Recognising that the emulsifying power of a soap is reflected in the fineness of dispersion of the oil globules in the resulting emulsion, Stamm[2] made a quantitative investigation of the dispersity of emulsions. He found that different monovalent soaps give the same mass maxima and also show the same total surface of dispersed globules. Such results do not favour the oriented wedge theory. As a matter of fact, the postulated packing of the oriented-wedge-shaped molecules of soap is only justifiable if the molecules were actually packed, and Stamm's calculations show this is not the case. Again, the work of Seifriz (see p. 245) cannot be reconciled with this theory. Finally, the theory cannot account for the observation of Finkle, Draper and Hildebrand that oleic acid, though soluble in benzene and not in water, gives an (unstable) emulsion of the unexpected type : benzene-in-water. Stamm reports a somewhat similar instance : "emulsions of amyl alcohol in water result regardless of which phase the soap is dissolved in, and from qualitative tests appear to give the same dispersity." Having quantitatively determined the inadequacy of the oriented wedge theory, Stamm[3] put forward an admittedly highly speculative theory based on electrical effects. Experimental work, however, is still necessary to test the theory.[4]

ROBERTS' THEORY OF EMULSIONS

A general theory of emulsions has been propounded by Roberts.[5] The aqueous phase usually contains dissolved or dispersed relatively highly polar material, which may be ionised. The " oil " phase is usually a complex mixture of liquid molecules of low polar moment, but dissolved or dispersed matter may be present of higher polar moments. The basis of the new theory is that the kinds and concentrations of ions and polar molecules determine emulsification.

It is postulated that the adsorption of ions in an interface increases as the ratio : charge/mass decreases. Molecules possess an unsymmetric distribution of electric charges, and therefore may be likened to a pair of ions in close proximity and constrained to move as a unit, but with reference to either end as bearing only a small charge. Hence, even with highly polar molecules, the ratio : charge/mass is very small in comparison with ions of even very large mass. This means that they will be adsorbed at an interface in preference to ions. (In all cases hydration or solvation results in ion or molecule complexes.) Orientation follows adsorption *on both sides of an interface,* there being an optimum range, as regards emulsifying efficiency, for the ratio of polar moment to molecular weight (see p. 127).

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[1] *J. Phys. Chem.*, **34**, 397 (1930).

[2] *Colloid Symposium Monograph*, **3**, 251 (1925).

[3] *Loc. cit.*, p. 262.

[4] For the most recent discussion on the oriented wedge theory, see Hildebrand, *J. Phys. Chem.*, **45**, 1303 (1941).

[5] *J. Phys. Chem.*, **36**, 3102 (1932).

It is suggested that an emulsifying agent, while not being "volumetrically" soluble in (say) water, may possess an "interfacial" solubility depending on the polarity of the molecule. For example, stearic acid is soluble in benzene and yet promotes the emulsification of benzene in water, *i.e.,* the emulsifying agent is not in the continuous phase. It is argued that the highly polar COOH end of the acid projects so far into the water phase that it is no stretch of the imagination to consider that the adsorbed acid molecules are really in the water phase with only their extreme ends projecting in the benzene.

Roberts' arguments lead to the conclusion that "the emulsifying agent can no longer be considered as a single material in one phase of the system, since the interfacial zone may consist of two Helmholtz 'double layers,' one in each phase, or it may consist of a 'compound' Helmholtz double layer, whose central portion consists of molecules, 'straddling' the interface."

The formation of a W/O emulsion is considered to occur as follows. At the moment the W/O interface forms, no adsorption has taken place, the electrokinetic potentials on either side of the interface are zero and the surface tensions on both sides of the interface possess their maximum dynamic values. The more mobile ions reach the interface in advance of the molecules, the ions of high polarity tending to accumulate in the interface on the oil side, the ions of low polarity on the water side. Ionic adsorption having reached equilibrium, the electrokinetic potentials are at a maximum. Meanwhile, the two surface tensions are decreasing very rapidly. Now the slower moving molecules compete for place in the interface, crowding out the ions and becoming oriented. Electrical equivalence will later be reached between the ions and polar molecules on the oil side, the corresponding electrokinetic potential being zero, and the surface tension will now only slowly decrease. In sufficient time the molecules will preponderate in the interface so that a static condition of a complete monomolecular layer of polar molecules in the primary layer is attained. Then the interfacial tension is at its minimum static value and the electrokinetic potential on the oil side will have acquired a low steady value, opposite in sign to that in the initial stages of the process.

The real emphasis in this theory is that electrokinetic potentials and surface tensions exist on *both* sides of the interface. His research has demonstrated the reversal of potential on the external oil side of the interface. His emulsions when fresh showed strong negative cataphoresis, which gradually became weaker, then ceased entirely and later changed to weak positive cataphoresis, the total time required being about eight weeks. These observations, it should be noted, were taken as the result of prediction by the theory. As regards the two interfacial tensions, experiments were made with the Du Noüy interfacial tensiometer, when frequently large differences were found between corresponding " push " and " pull " of the ring, although in the case of Nujol against distilled water the values coincided.

ZETA POTENTIAL AND STABILITY

Robinson[1] has drawn attention to the importance of the condensed monomolecular film in emulsion stability, following the observations of Harkins,[2] who showed that with sodium oleate as emulsifying agent a stable size distribution of globules was reached after an initial increase in size. At this point of stability the adsorption of the soap on the oil globules corresponded to a condensed monomolecular film.

Robinson argues that in such a case there will be a symmetrical distribution of ions on the surface of the globules, with orientation so that the paraffin tails are embedded in the oil and the lyophilic heads are directed to the water. With approach of the globules, the long chain ions (the negatively-charged heads of which mutually repel) will be redistributed, the ions slipping round the surface of the globules until there are comparatively few ions on the opposing faces. Hence, the zeta potential at that part of the surface of each globule approximating an approaching globule will be so lowered as to effect coalescence.

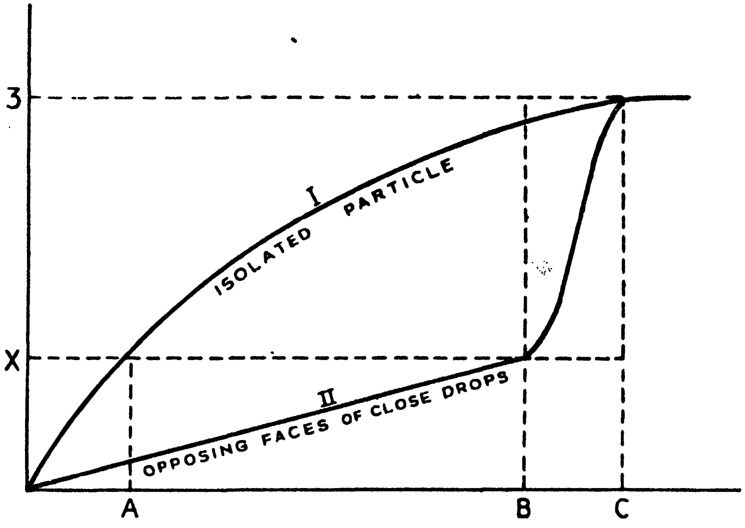

FIG. 35.

However, where there is a condensed film around the globules, ionic slip does not occur and there obtain the optimum conditions for stability. Possibly, a sufficiently concentrated ionic environment would equally serve. Referring to Fig. 35 by Robinson, it is reasoned that whereas the stability of a lyophobic sol depends on the zeta potential of the particles exceeding a certain critical potential X, which will be given by a comparatively low surface concentration A, the stability of an emulsion will not be governed by the zeta potential of the *isolated* globule (curve I) but by that on opposing faces of *neighbours* (curve II) which will only reach X at some higher concentration B. Only where the surface concentration reaches the value for a condensed monomolecular film will the zeta potential of an individual globule in the emulsion equal that at the opposing faces of neighbours.

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[1] *Trans. Faraday Soc.*, **32**, 1424 (1936).

[2] *J. Phys. Chem.*, **36**, 98 (1932).

"Hence when considering the stability of oil emulsions stabilised by paraffin chain ions, it is most important to determine the concentration of solution which will give a surface concentration which is nearly that corresponding to a condensed monomolecular film. This surface concentration will probably be attained with a solution concentration of paraffin chain electrolyte which gives the maximum lowering of interfacial tension. On the other hand, cataphoretic measurements will be of little interest, as these can only give the zeta potential of the isolated drops."

King [1] has discussed the electrical charge on emulsion globules and the chief interest of his results "is in the lack of relationship between electrical charge and stability." Thus, negatively-charged, saponin-stabilised emulsions were brought to the isoelectric state and to a positively-charged system, by the addition of aluminium sulphate. All the emulsions were stable for months. His conclusion, which we accept, is that "when no chemical reaction takes place between electrolyte and emulsifying agent, the electrical charge on the dispersed globules does not determine stability or type."

CASSEL'S THEORY

It is agreed that, where a film is concerned, the stability of an emulsion depends on the stability and impermeability of that film. The basic idea of a theory advanced by Cassel [2] is that emulsions can only be stabilised if the interfacial density of the interfacial films is greater for surfaces of larger than for those of smaller curvature.

"Since the film is in equilibrium with the adjacent phases, the thermodynamic potential of the emulsifying agent is the same through the whole system. This quantity is affected by the capillary pressure exerted upon the internal phase, and may be written in the form:

$$\mu_r = \mu_0 + \frac{2\sigma}{r(D_{in} - D_{ex})}.$$

Here μ and μ_0 designate the potential of the curved and the plane film respectively, σ the interfacial tension, r, the radius of the particle, D_{in} and D_{ex} the density of the emulsifying substance in the internal and the external phase respectively.

Since the film is stable only if $\mu_r < \mu_0$, it follows that D_{ex} must be larger than D_{in}. This is the well established rule of Bancroft, governing the inversion of emulsions. The thermodynamic theory also accounts for the fact that the stability will be increased by 'homogenisation,' that is, by decreasing the radius."

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[1] *Trans. Faraday Soc.*, **37**, 174 (1941).

[2] *Nature*, **137**, 405 (1936); *J. Phys. Chem.*, **42**, 475 (1938). See also Hildebrand, *ibid*, **45**, 1303 (1941).

STABILISATION WITH ELECTROLYTES

Cheeseman and King[1] have discussed the electrical double layer in relation to the stabilisation of emulsions with electrolytes, concentrated emulsions being prepared without the aid of surface-active materials. The qualitative results of their research are summarised by them as followes :—

(*a*) Certain electrolytes are capable of stabilising emulsions of water in polar organic liquids, or of polar organic liquids in water.

(*b*) The stabilising effect of the electrolytes is evident over a limited concentration range.

(*c*) The stabilities of the emulsions are dependent upon the electrolyte concentrations. A well-defined optimum concentration exists in every case.

(*d*) If the ions of potassium salts are arranged in the order of the decreasing stabilities which they are capable of imparting to an emulsion of water in amyl alcohol, we have :

CNS, I, NO_3, Br, ClO_3, Cl, SO_4.

(*e*) If the cations of divers chlorides be arranged in similar order, we have :

Sr, Cu, K, Li.

(*f*) The globules of the water in oil emulsions stabilised with electrolytes are positively charged, with those of the opposite type are negatively charged.

Taking the system amyl alcohol/water, the authors list 19 electrolytes which stabilise emulsions and 13 which do not. Stability measurements followed, the measure of stability being taken as the time required for the meniscus between the separated internal phase and the unbroken emulsion to pass from the 5 c.c. to the 15 c.c. graduation of an eudiometer tube containing the emulsion at controlled temperature. Fig. 36 shows the emulsion stability/electrolyte concentration curves for emulsions stabilised with halides of potassium, the corresponding curves in Fig. 37 being for the chlorides of Sr, Cu and K, all on a logarithmic scale.

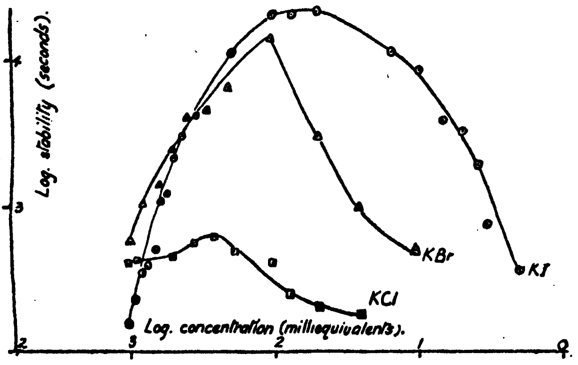

FIG. 36.

Interfacial tension measurements indicated no influence by the electrolytes. The stabilising powers of the anions follow their positions in the lyotropic series, otherwise their decreasing hydrophobic tendency. The most hydrophobic anions show the greatest power of emulsion stabilisation, effective within a limited range of concentration of the electrolyte. An appreciable solubility in amyl alcohol is noted so that at the boundary: amyl alcohol/water, such ions tend to collect on the alcohol side of the boundary, the more hydrophilic cations collecting in the aqueous phase. Thus a globule will bear at its surface the positive side of an electrical double layer, a factor towards stability of the emulsion.

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[1] *Nature*, **141**, 1099 (1938); *Trans. Faraday Soc.*, **36**, 241 (1940).

The authors' reasons for the changes in the stability of an emulsion consequent upon variations in the concentration of electrolyte are reproduced in full:

" Let us employ Gouy's conception of the diffuse ionic layer. Gouy imagined a plate, which, when placed in an electrolytic solution, assumed a charge and a definite potential relative to the liquid. Assuming the complete dissociation of the electrolyte, and considering the distribution of the positive and negative ions in the solution near the plate, he arrived at the expression :

$$a = \sqrt{\frac{\mathrm{DRT}}{4\pi \mathrm{N}^2\epsilon^2(n_a + n_c)\mathrm{N}_c n_c \text{ (or } \mathrm{N}_a n_a)}}$$

where a is the distance of the plate from the centre of gravity of the ionic atmosphere, ϵ is the charge on the ion, n_a and n_c are the valencies of the anion and of the cation, N_a and N_c are the numbers of gram ions in unit volume of this solution, and D is the dielectric constant of the solvent.

Now a may be taken as a measure of the effective thickness of the outer ionic layer. From the equation it follows that this thickness increases as (*a*) the dielectric constant of the solvent and the absolute temperature increase, and as (*b*) the ionic valencies and the ionic concentrations decrease.

An enlarged sphere of potency of the diffuse layer will tend to decrease the possibility of collision of two globules, and hence increase the stability of an emulsion. Here, then, is an explanation for the increase of the stabilities of our emulsions with decreasing electrolyte concentrations, in the section of the stability curve which extends from high concentrations to the optimum. It remains to consider the reasons for the falling off in stability when the concentration sinks below the optimum value, and for the differences in that value for different electrolytes.

At very low concentrations of electrolyte, the number of ions which cross from one phase to the other will be comparatively small, and the resultant effective charge on the globules will be insufficient to impart great stability to the emulsions. As the electrolyte concentration increases, the charge on the globule will be augmented. Simultaneously, in accordance with the law of Gouy, the effective thickness of the diffuse layer will decrease. There will thus come a time when the combined stabilising effects of the thickness of the diffuse layer and of the charge on the globule, will attain their resultant maximum. At this concentration, the emulsion formed from the two phases will exhibit its maximum stability.

By a continuation of such reasoning, there is no difficulty in explaining the shifting of the maximum in the stability/concentration curve which attends the changing of the anion. The more hydrophobic are the anions, the greater will be their migration into the oil phase, all other things being equal. As the charge on the globule depends upon the excess concentration of anions in the oil phase, the more hydrophobic anions will develop the most favourable relationship between the globule charge and the effective thickness of the double layer at lower electrolyte concentrations in the internal phase. The greater is the hydrophobic tendency of the anion, the less is the concentration of electrolyte for optimum emulsion stability. An examination of the stability curves will show that this is in concord with the experimental data.

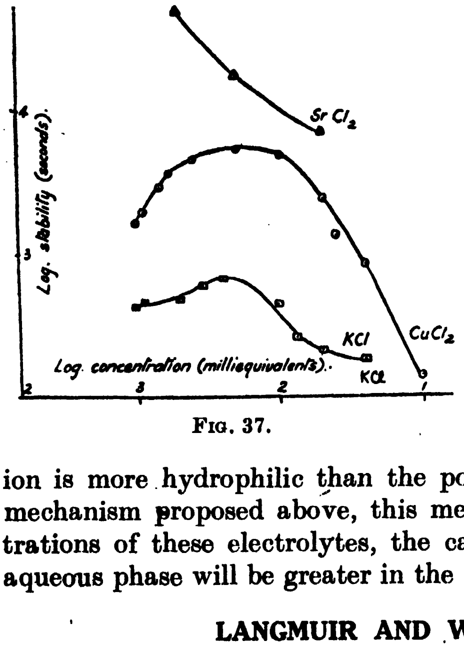

FIG. 37.

In the interests of simplicity, the *rôle* of the cation has not yet been considered. The nature of that ion has been shown to influence greatly the properties of the emulsions. The stabilising effect of the increased valency is at once apparent. Various cations of the same valency have, however, different effects on the stabilisation of emulsions. Thus, the optimum stability obtainable with NaI is considerably greater than that in the corresponding case with KI. It is generally held that the sodium ion is more hydrophilic than the potassium ion. With relation to the mechanism proposed above, this means that for corresponding concentrations of these electrolytes, the cationic impoverishment in the non-aqueous phase will be greater in the case of the sodium salt."

LANGMUIR AND WAUGH'S THEORY

Theoretically, O/W emulsions cannot be thermo-dynamically stable unless the interfacial tension (σ) between the two phases is zero. This is evident since the pressure in a globule of radius r exceeds that in the external phase by the amount

$$\Delta p = 2\sigma/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

On the coalescence of two globules the pressure within the globule decreases and there is a decrease in free energy. However, it is known that even when $\sigma = 0$, a stable emulsion can exist.

Langmuir and Waugh's argument [1] to explain the existence of stable O/W emulsions having an insoluble emulsifying agent adsorbed at the boundary of globules which have zero surface tension proceeds as follows.

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[1] *J. Gen. Physiol.*, **21**, 745 (1938).

The spreading [1] of an insoluble non-volatile substance as a monolayer at an air/water interface of surface area S is accompanied by a decrease in surface tension and is due to a spreading force F exerted by the adsorbed molecules as the two-dimensional analogue of a pressure. Here F is defined by

$$F = \sigma_0 - \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ_0 is the surface tension of the pure solvent and σ is that of the surface covered by the monolayer.

F is a function of the number (α) of molecules per sq. cm. in the monolayer and upon the temperature. The relation connecting these three quantities may be called an equation of state and is the two-dimensional analogue to the equation which relates the pressure with the density and temperature of a gas. Alteration of the free surface S still leaves the total number of adsorbed molecules, αS, constant and, in general, F increases rapidly as S decreases.

There is, however, a difference in the case of a solute which lowers the surface tension of water and forms an adsorbed film on the surface, since a decrease in free area S no longer means that αS be constant; solution of some adsorbed molecules occurs. Here, the Gibbs equation relates the properties of the adsorbed film to the concentration (c) of the dissolved solute:

$$dF/dlnc = \alpha kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

"By combining this with the equation of state so as to eliminate F it is possible by integration to obtain an 'adsorption isotherm' which gives α in terms of c and T. On the other hand, if we eliminate α we obtain an equation which we may call the 'force isotherm' that expresses F as a function of c and T."

Suppose an oil globule be surrounded by an aqueous solution of a substance which is adsorbable at the dineric interface. Then, α in equation (3) is positive and as c increases F increases (σ decreases). In those cases where it is possible to increase c to a point where σ is zero, no work is required to subdivide the globule. Although the total interfacial area is increased by such subdivision, σ remains zero since the extended interface adsorbs additional solute.

The authors now consider the case when the substance adsorbed at the oil/water interface is insoluble in both liquids. Suppose a globule of oil to have N molecules adsorbed on its surface S, whence:

$$\alpha = N/S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

With a sufficiently large value of N it is possible that F may be so great as to make $\sigma = 0$, which will occur if $F = \sigma_0$.

"It is now no longer necessary that the two phases should disappear. Consider, for example, a droplet of spherical form for which $\sigma = 0$. If the drop becomes distorted, its area increases and, therefore, α and F decrease and σ becomes positive. Any distortion of the drop from the the spherical form brings into existence a force which causes the drop to return to spherical form. If the amount of adsorbed substance is increased beyond that needed to make $F = \sigma_0$, or $\sigma = 0$, for the spherical drop, the drop will automatically increase its surface by assuming some non-spherical form, but σ remains zero."

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[1] See Brown, "Surface Tension of Film-Covered Liquids at Saturation," *J. Am. Chem. Soc.*, **55**, 4521 (1933).

The authors repeated experiments of Devaux, shaking together aqueous solution of egg albumen and benzene. The globules of benzene rise to the surface and coalesce to bulk phase, the protein going to the water/benzene interface. Here, with sufficient protein present, a cloudy appearance is noted due to minute folds of the protein membrane. If the albumen is used in a concentration of 10^{-3} parts by weight in the water, there is no such ready coalescence of the benzene globules. "They obviously have a very low surface tension, and a few drops are often seen which are drawn out into sharp points with a cloudy membrane over their surface, just as would be expected if the interfacial tension were zero. . . . . Since σ_0 for benzene/water is about 35 dynes/cm., the adsorbed protein film at the interface must be very highly compressed, and it seemed possible that at such high pressures irreversible changes occur like those observed at air/water interfaces causing F to decrease gradually below σ_0."

Further experiments were made with benzene brought to the density of water by addition of carbon tetrachloride. This mixture was shaken with 2 volumes of water. Then a few drops of a 1 per cent. aqueous solution of egg albumen were added, the tube gently shaken and allowed to rest. The hydrocarbon phase appeared as large drops, almost motionless, throughout the aqueous phase. Some of the drops were not even approximately spherical, their very irregular shape showing that the surface tension was actually zero.

MOLECULAR COMPLEX FORMATION

Important work on the stability of O/W emulsions has been carried out at Cambridge where Schulman [1] has followed up studies on molecular interactions in monolayers with similar studies at O/W interfaces.[2]

Injection of various substances under monolayers of cholesterol, gliadin, etc., spread on the surface of water, leads to molecular association. Two distinct phenomena were noted: (1) interaction limited between the polar groups of the monolayer substance and the injected compound causes adsorption of the latter on the monolayer coincident with changes in the surface potential and, occasionally, in the rigidity of the film; (2) when, superimposed on the polar attraction, strong association takes place between the non-polar parts of the two reacting species, there occurs a penetration of the monolayer coincident with changes both in surface pressure and surface potential. Stereochemical configurations of the reacting species profoundly affect the second phenomenon, interfacial molecular adlineation being assisted by suitable stereochemical relationship.

The importance of these observations to the study of emulsions lies in the phenomenon of penetration permitting extremely low values of interfactal tension and in the close parallel between the reactions at the air/water and O/W boundaries, the former already being well known from studies on surface films.

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[1] Schulman and Cockbain, *Trans. Faraday Soc.*, **36**, 651 (1940).

[2] Schulman and Rideal, *Proc. Roy. Soc.*, **B 122**, 29; 46 (1937).

The authors prepared emulsions of nujol and water with the aid of various emulsifying agents. Previous results by Schulman and Stenhagen[1] on the influence of non-polar steric factors on complex formation led to investigations of emulsions produced when the aqueous phase contained sodium cetyl sulphate and the nujol contained cholesterol, cetyl alcohol or elaidyl alcohol. The nature of the film at the air/water boundary, solid, viscous or liquid, was reflected in the character of the emulsion, grease, viscous or liquid. Thus, an excellent liquid emulsion of the O/W type resulted when 10 c.c. of nujol (containing 140 mg. cholesterol) where dispersed in 40 c.c. of water (containing 75 mg. Na cetyl sulphate).

The influence of polar interaction on complex formation and emulsion stability was next investigated. At the air/water boundary it had been noted that sodium cetyl sulphate rapidly penetrated a film of cholesterol to form a stable equimolecular complex, whereas only a negligible interaction was observed when the acetate or stearate of cholesterol was used instead of cholesterol itself. Similarly, the stability of molecular complexes at the O/W boundary is affected, as witness the failure to give stable emulsions when a mixture of cetyl sulphate and cholesterol stearate is employed. An excellent emulsion resulted when the reactants were cetyl sulphate and cholesterol.

Again, Schulman and Rideal[2] had observed that the injection of compounds of the type $C_{12}H_{25}X$, where $X =$ various polar groups, under cholesterol films at the air/water boundary gave a reactivity order of X towards the alcoholic group of cholesterol as :—

$$NH_3^{\cdot} > SO_4' > SO_3' > COO' > NMe_3^{\cdot} > \text{bile acid anions.}$$

This order of reactivity towards cholesterol was found to hold at an O/W boundary, with the stability of the emulsions dependent on the stability of the complexes between cholesterol and the various long chain polar compounds.

Very interesting is the effect of substituting for the long chain polar compounds substances having a polar group at each end of the chain.[3] Whilst sodium palmitate rapidly penetrates films such as cholesterol or octadecylamine to form stable complexes, sodium thapsate ($NaOOC[CH_2]_{14}COONa$) penetrates films of octadecylamine at an air-water boundary very poorly, to be easily squeezed out of the surface to form an adsorbed double layer underneath. With emulsion systems a similar condition holds. Whilst sodium palmitate + cholesterol promote fairly good nujol-in-water emulsions, sodium thapsate + cholesterol do not promote emulsions. Again, palmityl amidine + cholesterol promote fairly good emulsions, but not so cholesterol + palmityl diamidine. "This contrast between monopolar and dipolar

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[1] *Proc. Roy. Soc.*, **B 126**, 356 (1938).

[2] *Nature*, **144**, 100 (1939).

[3] See Cockbain and Schulman, *Trans. Faraday Soc.*, **35**, 716 (1939).

(polypolar) compounds has important biological implications. The latter compounds adsorb on to protein films but do not penetrate lipoid films. The monopolar compounds penetrate lipoid films readily."

Schulman and Cockbain now proceed to discuss the stability of nujol-in-water emulsions, mentioning that the one difference between nujol/water and air/water interfaces is that nujol causes an expansion of liquid films at the interface, although if the interfacial films are brought into a closely packed condensed state, all the nujol is eliminated from the interfacial monlayer.

We quote the authors as to the conditions to be satisfied to produce stable emulsions if complexes of certain types are formed at the oil/water interface, the cholesterol + cetyl sulphate complex being cited as example :—

(1) The complex must consist of at least two components, one of which is appreciably soluble in water, and the other appreciably soluble in oil, and the complex must be a stable one. Under these conditions, molecules of both types are held in the interface. The cholesterol cannot pull the cetyl sulphate molecules into the oil phase and the cetyl sulphate cannot pull the oil soluble cholesterol into the water. Since the complex remains stable when formed, only minute concentrations of each component are required to cover the oil/water interface and stabilise the emulsion.

(2) The interfacial tension must be negligibly small, so that the dispersion of the oil in the water phase involves as small an increase in free energy as possible.

(3) In conditions (1) and (2) the stability of the interfacial film and the interfacial tension lowering have both been stressed. These two factors depend markedly on the presence of an excess of the water soluble component under the equimolecular mixed film.

(4) The interfacial film must be a condensed liquid film, condensed because a high interfacial concentration of the complex is necessary, liquid because the film must be easily reformed on distortion.

(5) For O/W emulsions the oil droplets must be electrically charged. In fact, one of the chief actions of the complex is to crowd ions into the interface, since ions on their own repel one another, and thus yielding only vapour films at the interface.

MOLECULAR INTERACTIONS AT OIL/WATER BOUNDARIES

The remarkable results of Schulman and Cockbain (see p. 212) on nujol-in-water emulsions have been extended to the case of W/O emulsions.[1] Bearing in mind their postulates that two of the conditions for the promotion of O/W emulsions were (1) the presence of a film at the interface in the liquid condensed state, and (2) an electric charge on the film, we note their argument that in order to produce phase-inversion of such emulsions, the electric charge on the globules must be removed to result in breaking of the emulsion. Thereafter, inversion to the opposite type occurs if the composition of the two phases is such as to enable a solid condensed (preferably, an "inter-linked" solid condensed) film to form at the interface.

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[1] *Trans. Faraday Soc.*, **36**, 661 (1940). See also Woodman, *J. Soc. Chem. Ind.*, **53**, 115 T (1934).

Results are recorded where heptadecylamine is dissolved in nujol and shaken with an equal volume of 0·01 NHCl, to yield a poor O/W emulsion to which various salts and acids were added. It is concluded that a rigid, or at least very viscous, film at the interface favours the W/O type of emulsion. Further, the interfacial film should be uncharged.

Some results with tannic acid are of much interest, since its addition to the heptadecylamine HCl nujol emulsion leads to an O/W emulsion at *p*H 2 and a W/O emulsion at *p*H 7 to 8. Moreover, the change in emulsion type as a result of *p*H adjustment is a reversible phenomenon. The authors had already shown that at *p*H 2 tannic acid reacts only weakly with long-chain amine films at an air/water interface, the amine film remaining liquid and ionised. Hence, the O/W type of emulsion at this *p*H value. In the range *p*H 7 to 8, tannic acid reacts strongly with an amine film, converting it from a liquid to a rigid solid state, hence the W/O system.

The two conditions for promoting W/O emulsions are also applicable to the use of negatively charged soaps as the emulsifying agents, the requirements being fulfilled when long-chain carboxylic acid molecules are inter-linked at the O/W interface by polyvalent metal ions.

Conditions for the *direct* preparation of W/O emulsions are that the emulsifying agent be brought to the O/W interface to yield a film, rigid and uncharged. An excellent illustration is provided by the use of digitonin + cholesterol, neither substance alone being capable of stabilising nujol/water systems. However, when an aqueous solution of digitonin is mixed with a nujol solution of cholesterol, stable W/O emulsions are formed due to the strong complex formation at the liquid/liquid interface. If, instead of digitonin, there be employed an acid saponin, the O/W type of emulsion is formed, the interfacial film being viscous liquid and negatively charged.

The extension of this work to dual emulsions and the inversion of phases is discussed elsewhere (see p. 249).

SOLIDS IN THE DINERIC INTERFACE

So unexpected a substance as solid NaCl is capable of stabilising emulsions of $CHCl_3$ in brine-saturated solutions of Löffler methylene blue.[1] Solid NaCl is witnessed around the globules. Numerous other solids are named as emulsifying agents in the scientific and in the patent literature.

Powdered $CaCO_3$ settles more rapidly in moist than in dry benzene. With the two bulk liquids the $CaCO_3$ goes to the interface; if shaken, the benzene forms globules protected by hydrated solid.[2] The addition of a small amount of oleic acid reverses the emulsion. Again, $BaSO_4$ in the system : heptane/$SeOCl_2$ settles completely below the interface and will not form an emulsion ; in the system : 70 per cent. $H_2SO_4/SeOCl_2$, the $BaSO_4$ lies on top of the interface, and no emulsion forms. In the system : heptane/water, $BaSO_4$ goes into the interface and stabilises emulsions of the O/W type.[1] Reinders [2] described the disposition of 15 solids at 5 interfaces and Davis and Curtis [3] 15 solids at 25 interfaces. Photomicrographs of emulsion globules showing the disposition of solid particles at the interfaces have been published by Scarlett, Morgan and Hildebrand.[4] Such qualitative observations have recently received detailed investigation from the standpoint of wetting and the importance of the angle of contact.

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[1] Liesegang, *Kolloid-Z.*, 45, 370 (1928). Powdered NaCl also stabilises emulsions of heptane in aniline.

[2] Talmud, *Z. physik. Chem.*, Abt. A, 142, 233 (1929); 146, 315 (1930); Talmud and Suchovolskaya, *Kolloid-Z.*, 55, 48 (1931); Devaux, *Compt. rend.*, 197, 105 (1933).

ANGLES OF CONTACT

When a drop of liquid rests in equilibrium on the surface of a solid it meets the solid at an angle which is termed the angle of contact. This is the angle between the surface of the liquid and the solid-liquid interface. Young's equation for this equilibrium state is : $\sigma_1 - \sigma_{1,2} = \sigma_2 \cos \theta$.

where σ_1 = surface tension, solid/air,
$\sigma_{1,2}$ = ,, ,, solid/liquid,
σ_2 = ,, ,, liquid/air,
θ = angle of contact.

Complete wetting of the solid indicates zero angle of contact ; the contrasting case of complete non-wetting would have a contact angle of 180°. An extensive literature concerns the measurement of the angle of contact,[5] its dependence on the condition of the solid surface, the difference between the advancing and the receding angles,[6] and the time of contact between the solid and liquid.[7]

The interfacial angle of contact is that angle obtaining when a solid meets the interface between two immiscible liquids, and it has profound importance for the theory of emulsions stabilised by solid particles.

Obviously if the solid (conveniently considered as a sphere) meets the interface with this in line with its own equator, the angle of contact is exactly 90°. The solid would then possess no preferential attraction for either of the liquids. It is practically a hypothetical case.

Referring to Fig. 38, consider the disposition of a solid in relation to a liquid/liquid system, oil/water, in terms of the various interfacial tensions operating. Three cases arise :

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[1] Lehner and Taylor, *J. Phys. Chem.*, **28**, 962 (1924).

[2] *Kolloid-Z.*, **13**, 237 (1913).

[3] *Ind. Eng. Chem.*, **24**, 1137 (1932).

[4] *J. Phys. Chem.*, **31**, 1566 (1927).

[5] Langmuir, *Trans. Faraday Soc.*, **15**, 71 (1920) ; Nietz, *J. Phys. Chem.*, **32**, 255, 620 (1928) ; Green, *ibid.*, **33**, 921 (1929) ; Sheppard and Newsome, *ibid.*, **39**, 143 (1935); Herstad, *Kolloid-Z.*, **55**, 169 (1931) and **64**, 6 (1933) ; Schultze, *ibid.*, **62**, 294 (1933) ; Haller, *ibid.*, **53**, 247 (1930) ; **54**, 7 (1931) ; **55**, 1 (1931) ; Lambert, *ibid.*, **60**, 3 (1932) and *Klin. Wochschr.*, **11**, 727 (1932) ; Adam and Jessop, *J. Chem. Soc.*, **1925**, 1863 ; Adam and Morrell, *J. Soc. Chem. Ind.*, **53**, 255 T. (1934) ; Cox, Wark and Wark, *Nature*, **129**, 871 (1932) ; Valentiner, *Physik. Z.*, **15**, 425 (1914) ; Talmud and Lubman, *Z. physik. Chem.*, **Abt. A**, **148**, 227 (1930) ; Tritton, *J. Soc. Chem. Ind.*, **51**, 299 T. (1932).

[6] Ablett, *Phil. Mag.*, **46**, 244 (1923) ; Bartell and Wooley, *J. Am. Chem. Soc.*, **55**, 3518 (1933) ; Bartell and Merrill, *J. Phys. Chem.*, **36**, 1178 (1932).

[7] Pockels, *Kolloid-Z.*, **62**, 1 (1933).

(1) If $\sigma_{s,o} > \sigma_{s,w} + \sigma_{w,o}$ the solid will suffer complete immersion in the water phase.
(2) If $\sigma_{s,w} > \sigma_{s,o} + \sigma_{w,o}$ the solid will suffer complete immersion in the oil phase.
(3) If $\sigma_{w,o} > \sigma_{s,o} - \sigma_{s,w}$ the solid will be distributed in the dineric interface.

Since one of the liquids will exhibit preferential wetting of the solid, the equation for equilibrium becomes : $\sigma_{s,o} - \sigma_{s,w} = \sigma_{w,o} \cos \theta$. If $\sigma_{s,w} < \sigma_{s,o}$ then $\cos \theta$ is + and θ is < 90°. The greater portion of the solid is then surrounded by the water so that its equator lies in the water phase. Similarly, if $\sigma_{s,o} < \sigma_{s,w}$ then $\cos \theta$ is negative and θ is > 90°, the major portion of the solid being surrounded by the oil phase.

Early work on the concentration of dissolved substances at various dineric interfaces was done by Wilson,[1] Swan,[2] von Lerch,[3] and Tomlinson.[4] Hofmann [5] investigated the concentration of small solid particles at the interface between chloroform and water, using finely-divided red lead. When this solid is shaken with chloroform and water the chloroform droplets become coated with red lead, and so are kept emulsified in the water phase. Hofmann's explanation, following ideas expressed by Des Coudres,[6] is to the effect that, when a finely-divided solid is preferentially wetted by water more than by chloroform, the water will displace chloroform and form an aqueous film around the particles of the solid, which will tend to remain in the aqueous phase owing to the fact that work must be done to effect their removal therefrom. In the case of an organic liquid heavier than water, like chloroform, the solid particles will remain in the water, except for those whose size necessarily makes them sink under gravitational force. With a liquid such as

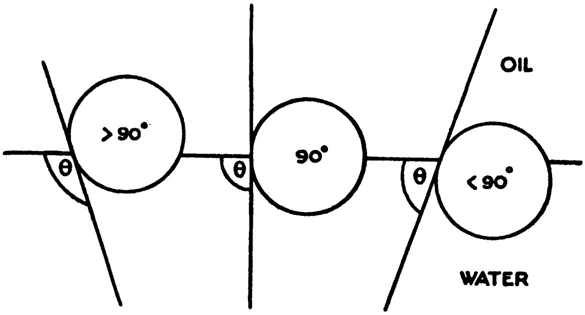

FIG. 38. Possible arrangements of a solid emulsifying agent at an oil/water interface.

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[1] *J. Chem. Soc.*, **1**, 174 (1848).
[2] *Phil. Mag.*, **33**, 36 (1848).
[3] *Drude's Ann.*, **9**, 434 (1902).
[4] *Phil. Trans.*, **161**, 51 (1871).
[5] *Z. physik. Chem.*, **83**, 385 (1913).
[6] *Arch. Entwicklungsmechanik.*, **7**, 325 (1898).

benzene—lighter than water—the particles will all remain in the water phase.

An extension of this rule is that if the chloroform or benzene wets the solid more strongly than does water, globules of water will persist, surrounded by solid particles, and all suspended in a continuous phase of chloroform or benzene.

In 1910, Pickering[1] asserted that, while high viscosity and low surface tension are undoubtedly favourable to emulsification, the most important factor is the presence of finely-divided particles, insoluble in the external phase, which coat the oil globules, and so prevent their coalescence.[2] Donnan[3] criticised this "solid particle theory," stating that Pickering apparently did not connect adsorption with the lowering of surface tension, and that electrical effects were entirely overlooked.

Pickering's emulsions, however, although in many cases stabilised by insoluble powders, do not form exceptions to Donnan's surface tension theory, since the solid particles would not go to the oil/water interface unless this new arrangement was accompanied by a lowering of the oil/water interfacial tension.

Pickering stated that solid emulsifiers must be of a certain definite range of grain,[4] non-crystalline, and *more readily wetted by water than by oil* (for O/W emulsions).

A solid particle in the interface between two immiscible liquids meets that interface with a constant angle of contact. If now the interface is curved in such a sense as to enclose the more poorly wetting liquid, in order to keep this angle constant, the line of contact must move over the surface of the solid so as to increase the area wetted by the better wetting liquid. A reverse curvature of the interface will decrease the area covered by this liquid, and consequently the former arrangement will be more stable. The type of the emulsion promoted will, therefore, be such that the liquid which wets the solid preferentially forms the external phase.[5]

ADHESION TENSION

Intensive study of the wetting of solids by liquids has been made recently,[6] notably by Bartell[7] and his associates. With Osterhof[8] he described a method for the determination of the degree of wetting of a solid by a liquid, based on the measurement of the pressure with which one liquid will displace another liquid from a powdered material which has been compressed within a cylinder.

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[1] *Kolloid-Z.*, **7**, 11 (1910).

[2] Similar views in favour of his "Particulate Theory" of emulsions were advanced by Marshall (*Pharm. J.*, **28**, 264 (1909)). He stated, however, that the theory only held in certain instances.

[3] *Kolloid-Z.*, **7**, 214 (1910).

[4] *J. Soc. Chem. Ind.*, **29**, 129 (1910).

[5] See van der Minne, "Over Emulsies" (Amsterdam, 1928), p. 64; Ramsden, Clayton's "The Theory of Emulsions and Their Technical Treatment" (London, 1928), Appendix, p. 229; Fain and Snell, *Ind. Eng. Chem.*, **31**, 48 (1939), on "Surface Activity of Solid Emulsifiers."

[6] Talmud, *Z. physik. Chem.*, **Abt. A. 156**, 237 (1931); Berl and Schmitt, *Kolloid-Z.*, **61**, 80 (1932); **63**, 327 (1933); **65**, 93 (1933).

[7] Summarised by Bartell in Alexander's "Colloid Chemistry," Vol. 3 (New York, 1931), p. 41.

[8] *Ind. Eng. Chem.*, **19**, 1277 (1927); *J. Phys. Chem.*, **34**, 1399 (1930); **37**, 543 (1933); *Colloid Symposium Monograph*, **5**, 113 (1928). An improved technique is described by Bartell and Jennings, *J. Phys. Chem.*, **38**, 495 (1934). See also Bartell and Bartell, *J. Am. Chem. Soc.*, **56**, 2205 (1934). Important papers on the preferential wetting of solids by liquids are given by Davis and Curtis, *Ind. Eng. Chem.*, **24**, 1137 (1932) and Buckley and Snyder, *J. Am. Chem. Soc.*, **55**, 194 (1933).

Freundlich [1] had defined the *adhesion tension*, A, as the difference between the interfacial tensions of the solid :

$$A_{s,o} = \sigma_s - \sigma_{s,o} = \sigma_o \cos \theta$$

where $A_{s,o}$ = the adhesion tension of an organic liquid against the solid. Provided that the contact angle formed by a liquid/air/solid system is greater than zero, this equation permits the determination of the adhesion tension by measuring the surface tension of the liquid and the angle of contact. Usually, however, the contact angle is zero and the adhesion values cannot be determined. Bartell and Osterhof, therefore, made use of the following formulation :

$$A_{s,w} - A_{s,o} = \sigma_{s,o} - \sigma_{s,w} = \sigma_{o,w} \cos \theta_{o,w}$$

where $A_{s,w}$ = the adhesion tension of water against the solid, and
$\theta_{o,w}$ = the interfacial contact angle between the dineric interface and the solid.

With the value $A_{s,o}$ determined for a single liquid from the first equation it becomes possible, by measuring $\sigma_{o,w}$ and $\theta_{o,w}$ to determine $A_{s,w}$ from the second equation. This done, the adhesion tension of other organic liquids against the solid could be obtained by employing the same equation and again determining the interfacial tensions and the contact angles of these other water/organic liquid/solid systems.

Given the adhesion values of a solid and various liquids, fairly accurate prediction is possible of the relative stability of suspensions of the solid in these liquids. Stability will be most noticeable in that liquid possessing the highest adhesion tension for the solid. Where the values are low, the tendency is towards flocculation. When the suspension is present in a system of two immiscible liquids, the solid will tend to immersion in that liquid which gives the highest adhesion tension with the solid.[2]

Bartell and Miller [3] investigated the degree of wetting of silica by crude petroleum oils ; the adhesion tension of the various oils against silica ranged from 58·87 to 72·68 dynes/cm. Later,[4] they showed that effective displacing agents appear to be those that alter the aqueous solution/silica interface, either through a high degree of adsorption or through chemical reaction at the interface. The adhesion tension values of various carbon blacks against water were found as 65·96—82·40 dynes/cm., and against benzene as 40·72—55·55 dynes/cm.

The relation of adhesion tension to the absorption of liquid by powdered solids (cf. oil absorption value of pigments) has been discussed by Bartell and Greager.[5] Liquid absorption values were determined for three powdered solids with a series of different liquids. A similar linear relationship was observed between liquid absorption and adhesion tension for all those systems in which the liquid forms a zero angle of contact against the solid. The liquid absorption was least for those liquids which showed the highest adhesion tension against the solid. For those systems in which the liquid formed a finite contact angle against the solid the liquid absorption was lower than would be expected from the foregoing relationship. The larger the angle of contact (and the less the adhesion tension) the less was the oil absorption.

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[1] " Colloid and Capillary Chemistry " (London, 1926), p. 157.
[2] See Bechold and Schnurmann, *Z. physik. Chem.*, Abt. A. 142, 1 (1929).
[3] *Ind. Eng. Chem.*, 20, 738 (1928).
[4] *Ibid.*, 24, 335 (1932). See also Bartell and Smith, *ibid.*, 21, 1102 (1929).
[5] *Ibid.*, 21, 1248 (1929).

An extension of this research was made by Bartell and Hershberger,[1] who investigated the relation of liquid absorption with a series of organic liquids to the interfacial tension of these liquids against water. The authors' summary of results states that the liquid absorption values of a series of zero contact angle liquids with polar solids increase linearly with increase in interfacial tension values of those liquids against water. The liquid absorption values of a series of zero contact angle liquids with carbon (a non-polar solid) decrease linearly with increase in interfacial tension values of these liquids against water. The order of decrease in free surface energies which occurs when a polar solid is wetted by each of a series of zero contact angle liquids is the same as the order of the decrease in free surface energies which occurs when water is brought into contact with the same series of liquids. The liquid absorption values of contact angle liquids with any solid bear no apparent relationship to the interfacial tension values. They are much lower than liquid absorption values obtained when zero contact angle liquids of corresponding interfacial tension values are used.

It was observed that liquid absorption by a given solid powder is approximately proportional to the specific surface. Powders with the same specific surface but of different materials may show different liquid absorption values indicative of specific but different forces of adhesion between a given liquid and the different solids.

A microscopic method for the measurement of interfacial contact angles was used by Bartell and Merrill [2] to check the method of Bartell and Osterhof, who had used a cell with an inlet tube at one end and an attached manometer at the other. In one half of the cell was packed water-wet solid and in the other half the organic liquid-wet solid. Employing silica as the powder, the water tended to displace the organic liquid from the powder and thereby set up a pressure. On the assumption that the pores of the powder served as a multiple capillary system, and also assuming that an equilibrium contact angle was formed in each of the pores, the value of this contact angle was obtained from the equation :

$$\cos \theta_{w,o} = g \frac{\mathrm{P}r}{2} \sigma_{w,o}$$

where g = gravity constant,
P = manometer pressure in grm./cm.^{2},
r = average effective radius of all capillaries.

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[1] *Ind. Eng. Chem.*, **22**, 1304 (1930).

[2] *J. Phys. Chem.*, **36**, 1178 (1932). See also Bartell and Whitney, *ibid.*, 3115 (1932).

The direct measurement of interfacial contact angles substantially confirmed the results gained indirectly by the pressure of displacement method. Accordingly, it is believed that the formulations used in the determination of adhesion tension are justified.

THE SOLID/LIQUID INTERFACE

Harkins and his co-workers have also carried out a series of investigations on the solid/liquid interface, studying particularly sedimentation and flocculation of powders in liquids. Harkins and Gans [1] point out that the energy of immersion of a solid oxide powder is quite small in such non-polar liquids as hexane, C_6H_6, or CCl_4. Addition of a small quantity of an organic compound such as organic acid, alcohol or amine causes the heat of immersion to be much increased. They designate molecules of this type as hetero-homopolar. Data relating to heat of immersion agree with the idea that the polar groups of the hetero-homopolar molecules are oriented towards the oxide at the solid/liquid interface. Experiments were made to ascertain the effect of such an oriented interfacial film upon the final sedimentation and upon the rate of sedimentation of a powder in a liquid, these phenomena serving to indicate the degree of flocculation of the powder.

The authors found that the presence of a monomolecular oriented film of molecules of the hetero-homopolar type prevents flocculation. Should water be also present, the mixed film is less able to prevent flocculation ; sufficient water present in the mixed film leads to flocculation as pronounced as in a pure non-polar liquid.

It is emphasised that the correlation of extent of sedimentation with energy of wetting is not a simple one. For example, titanium oxide exhibits a high energy of immersion with both oleic acid and water and a low energy with benzene, yet oleic acid in benzene deflocculates the suspension, while if water is added, the suspension becomes re-flocculated. Electrical relations at the solid/liquid interface cannot be ignored, and the energy of adhesion and of cohesion may also be involved.

The work of Harkins and Dahlstrom [2] on the wetting of pigments and other powders showed that the energy relations at the solid/liquid interface in the case of oxides and organic liquids were similar to those between water and the same organic liquids, but the polar groups are more strongly attracted to the solid than to water. Experiments by Ryan, Harkins and Gans confirmed this.

Similar results by Bartell and Walton [3] showed that the degree of packing of a powder upon sedimentation is most pronounced in that liquid against which it possesses the maximum adhesion tension, and is progressively less in those liquids against which it has a progressively lesser adhesion tension. Their research demonstrated that the surface properties of stibnites could be altered by simple heat treatment. It was possible to cause surfaces to function either as hydrophobic or hydrophilic surfaces [1] and, interesting to note, it was possible to reduce surfaces to a condition in which they showed no selective wetting tendency, *i.e.*, they were preferentially wetted neither by water nor by organic liquids.

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[1] *J. Phys. Chem.*, **36**, 86 (1932).

[2] *Ind. Eng. Chem.*, **22**, 897 (1930) ; cf. Ryan, Harkins and Gans, *ibid.*, **24**, 1288 (1932).

[3] *J. Phys. Chem.*, **38**, 503 (1934).

An important extension of this research was carried out by Bartell and Hatch [2] when they showed that galena apparently functioned either as an organophilic or as a hydrophilic solid depending upon whether it is first wetted by an organic liquid or by water. The significance of this finding is that it should be possible by the aid of galena to prepare emulsions of both the O/W and W/O types, according to whether the powder was first wetted by water or by oil.

Having indicated that modern work has centred round the qualitative and quantitative preferential wetting of solids by water and organic liquids,[3] it now remains to present the only fully developed theory of the promotion and stability of emulsions by the aid of solid powders as emulsifying agents.

RAMSDEN'S THEORY OF EMULSIONS

For the second edition of the present book, Ramsden provided an appendix giving an account of his theories relating to emulsions stabilised by bulk-solid particles. For the third and present editions he has written the following shorter and amended account as being sufficient to show the main features of those theories :—

(1) When two "immiscible" bulk-liquids W and O are in mutual contact, a portion of each liquid near the WO interface is anisotropic and is acted on by a "simple" surface-tension. These portions are termed the W(O) and O(W) "surface-zones," and have opposite electric charges. Their specific thicknesses are $z_{W(O)}$ and $z_{O(W)}$. Both zones taken together make the duplex WO "surface-region." The thickness of a surface-zone is usually considerably greater than the maximal distance from the interface to which any direct intrinsic action of the bracketed liquid across the interface extends into the liquid which forms the surface-zone. The algebraic sum of the simple surface-tensions $T_{W(O)} + T_{O(W)}$ constitutes the "duplex" surface-tension T_{WO}. A simple surface-tension may be either "positive" (*i.e.*, a contractility) or "negative" (*i.e.*, an expansility).

(2) When a liquid L and a solid S are in mutual contact, the liquid has an isotropic "interior," a definable L(S) surface-zone and a surface-tension $T_{L(S)}$ which is of constant magnitude where the solid in contact with the L(S) zone has constant configurations. $T_{L(S)}$ is moreover a "*free*" surface-tension, since it acts on molecules which are free to migrate from any one position to any other position in the liquid, and is accordingly able to produce surface-parallel contraction or expansion of the L(S) zone.

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[1] See Berl and Schmitt, *Kolloid-Z.*, **68**, 350 (1934); Il'in and Vassiliev, *Z. physik. Chem.*, Abt. A., **158**, 365 (1932).

[2] *J. Phys. Chem.*, **39**, 11 (1935).

[3] Heats of wetting of solids by liquids are discussed by Rehbinder and Krajuschkina, *Z. physik. Chem.*, Abt. A. **142**, 282 (1929) and Stenzel, *J. Am. Chem. Soc.*, **54**, 870 (1932).

The solid, on the other hand, has no definable surface-zone or necessarily isotropic interior or necessarily constant configurations in its superficial volume-elements, and it is questionable whether, when the interface is plane, its superficial volume-elements have of necessity any tendency whatever to contract or expand in surface-parallel directions. It is, moreover, certain that any such tendency would be neither necessarily constant nor "free" to act. A solid phase has, in short, no such surface-tension as $T_{S(L)}$. There is, accordingly, no such surface-tension as T_{SL}, nor are there any such surface energies as could properly be designated $T_{S(L)}$ or T_{SL}.

(3) When a WO interface meets a plane face of a bulk-solid S at a WOS "line of intersection," the WO, W(S) and O(S) surface-zones terminate in a WO(S) "insertion-zone." A plane tangent to the line where the ordinary WO interface passes into the insertion-zone forms with the face of the solid the supplementary angles of contact $\theta_{W(O)}$ and $\theta_{O(W)}$. The insertion-zone treated as a whole is in equilibrium under the actions exerted on it by its environment. Resolving along a solid-parallel axis at right angles to the line of intersection all the actions exerted on unit length of the insertion-zone, and making the not *strictly* correct assumption that the action of the solid is exerted at right angles to the face of the solid, the equilibrium demands the equation :

$$T_{WO} \cos \theta_W + T_{W(S)} - T_{O(S)} = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

True variability of θ_W is, of course, due to variability in the solid phase. The differences between this and the corresponding classical equation :

$$T_{WO} \cos \theta_W + T_{SW} - T_{SO} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

although formally slight, have very considerable significance.

(4) A positive L(S) zone (*i.e.*, one in which $T_{L(S)}$ is positive) surrounding a spherical bulk-solid particle S suspended in a liquid L exerts radial thrusts on the solid ; a negative L(S) zone exerts radial tractions. When, by approximating two similar solid particles until the distance between them is less than $2z_{L(S)}$, their L(S) zones are made to "overlap," the radial thrusts or tractions exerted by the liquid on the near aspects of the solids become less than those exerted on their remote aspects. Hence, if $T_{L(S)}$ is positive, the particles tend to be thrust closer together, and if $T_{L(S)}$ is negative, tend to be dragged further apart. Another result of the overlapping is that the thinned "sandwich-liquid" tends to be dragged out if $T_{L(S)}$ is positive, but to be thickened by a thrusting in of fresh molecules if $T_{L(S)}$ is negative. For distances between the particles greater than some very small distance x (conjectured to be approximately that of a bimolecular sandwich), the above tendencies are the only ones that need be considered.

Similar considerations are applicable when the W(O) zones surrounding two "naked" globules of a pure liquid O suspended in a pure liquid W are made to overlap, but they must be supplemented by consideration of the changes in the O(W) zones and therefore of the duplex tension T_{WO} in the WO surface-region subtending the overlap. If the W(O) zones are positive, T_{WO} will decrease progressively as the overlap spontaneously progresses, and the WO interfaces subtending the overlap will bulge out more and more until they meet, whereupon its globules will coalesce to form one spherical globule. If the W(O) zones are negative, T_{WO} will at first increase as the overlap is forcibly increased (by external agency) and the WO interfaces will at first become less convex towards each other, but with greater overlap a stage will be reached when T_{WO} begins to decrease and the WO interfaces begin to bulge towards each other. Given two emulsions made from the same pair of equally viscous liquids W and O devoid of any third substance, one emulsion of W in O type, the other of O in W type, both having equally numerous bulk-liquid globules of the same size, it is concluded that the type in which the globules consisted of the liquid which had the larger simple tension at the WO interface would be the less unstable.

(5) A bulk-solid particle adsorbed at a WO interface is termed a "stud." It is considered to be a bulk-solid if it is large enough to have a W(O) "stud-cap," an O(W) stud-cap and a girdle of WO(S) insertion-zone between them. A sphere with diameter exceeding 100×10^{-7} cm. would probably satisfy these requirements. In the W, O, S, emulsion-systems considered, all the studs will be supposed similar spheres, all the globules, whether of W in O type or O in W type, will be similar but very much larger spheres, and the densities of W, O, and S will be supposed nearly equal. Each study has a W "pole," an O "pole," and an "equator." To conform with equation (1) the insertion-zone must lie between the equator and whichever pole is in the "obtuse-angle liquid," *i.e.*, the liquid inside which θ is an obtuse angle (the "less-wetting" liquid as it might be termed). Hence, if O is the "obtuse-angle liquid," the O(S) stud-cap is smaller than the W(S) cap, and $T_{O(S)}$ is algebraically greater than (*i.e.*, more positive or less negative than) $T_{W(S)}$.

A globule is "stud-saturated" when no additional stud can be adsorbed. It is impossible to discuss here the various factors which determine the saturation-stud-interval, and the advances or retreats of the WOS line of intersection along the surfaces of the studs which would attend the adsorption of fresh studs while saturation is being attained. It must suffice merely to point out that the globule-tangential tractions exerted on the WO(S) insertion-zones (or what remains of these zones) by T_{WO} (or what remains of this tension) tend to approximate the studs, and that the simultaneous overlapping of negative W(S) or O(S) zones tends to separate the studs. The saturation-stud-interval must hence be greater in some of these cases than in cases where the W(S) and O(S) zones are positive, a conclusion which has obvious bearings on the contrast between the surface rigidity of aqueous solutions of saponin and the surface-mobility of those of sodium oleate.

Fig. 39 shows a stud-saturated globule made of the "obtuse-angle-liquid" O, a globule of type 1. Fig. 40 shows a globule of the "acute-angle-liquid" W, a globule of type 2. Note (*a*) that the WO interfaces are well protected in type 1, but much more exposed in type 2; (*b*) that the work required to "desorb" a stud by thrusting it into the interior of the globule is much greater in type 1; (*c*) that a type 1 globule would adsorb more studs at the same stud-interval than would one of type 2, and would also have a smaller area of WO interface : (this would have been more evident if the globules and studs of Fig. 39 had been of the same sizes as in Fig. 40) ; (*d*) that the elastic springs constituted by T_{WO} tend to approximate the internal stud-poles of type 1, but the external stud-poles of type 2. A stud-saturated WO surface region would hence tend to become concave towards the obtuse-angle-liquid.

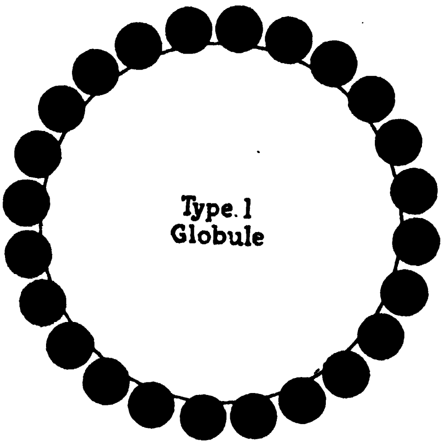

FIG. 39. Stud-saturated globule of the obtuse-angle-liquid, O (Ramsden).

(6) Stability of emulsions. The effects of progressively approximating equal-sized similar globules saturated with equal-sized studs, equal in all the cases compared, depend on the signs and magnitudes of $T_{O(S)}$, $T_{W(S)}$, $T_{O(W)}$ and $T_{W(O)}$ and on the size of the saturation-stud interval and on the rates of change of these quantities. They depend also in cases where approximation is not spontaneous on the magnitude of the approximating force applied ab extra. Assuming that no stud is large enough to have *two* WO(S) insertion-zones, it must suffice to consider the following six cases. In all of them O is the obtuse-angle-liquid, T_{WO} is the same tension and θ_W is supposed to be very obtuse, say 135°. The fact that it is obtuse requires $T_{O(S)}$ to be algebraically greater than $T_{W(S)}$.

A1 and A2, both $T_{O(S)}$ and $T_{W(S)}$ positive.

B1 and B2, $T_{O(S)}$ positive and $T_{W(S)}$ negative.

C1 and C2, both $T_{O(S)}$ and $T_{W(S)}$ negative.

The numerals denote the type of globule.

In cases A1, A2 and B2 the external stud-caps are positive and the globules would tend to closer approximation. In the cases B1, Cl and C2 the external stud-caps are negative and the globules would have to be forced into closer approximation by some external agency, such as creaming, sedimentation, or convection currents.

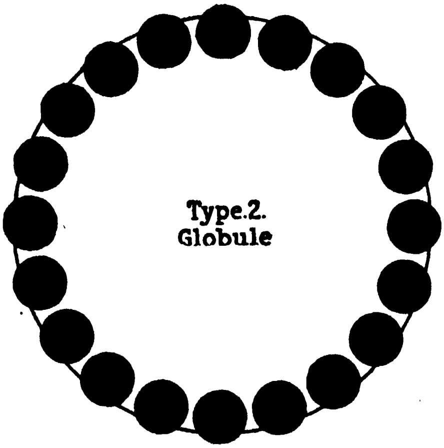

FIG. 40. Stud-saturated globule of the acute-angle-liquid, W (Ramsden).

The conclusions reached are (*a*) that in A, A2 and B2, emulsions of such globules would be absolutely unstable ; (*b*) that for emulsions of two equally viscous liquids, under ordinary laboratory conditions subjected to no violent mechanical disturbance, those of B1 and C1 globules would be very stable, but those of C2 globules would in some cases be stable, in most cases unstable, and in all cases very much less stable than those of C1 with which alone they can fairly be compared.

(7) Two general conclusions are based upon the theoretical considerations stated above.

Firstly, no ordinary emulsion can be stabilised by bulk-solid particles unless the continuous "external" liquid is one which has a negative "simple" surface-tension where it is in contact with the solid particles.

Secondly, of the two types of emulsions which might conceivably be made from a given pair of liquids and a given solid powder the type in which the contact-angle made against the solid particles is obtuse inside the globules is so much more stable than that in which the corresponding contact-angle is acute that the emulsion actually prepared would always have the obtuse contact angles inside the globules.

Ramsden and Brooks had tested (1922–23) the validity of this "angle-of-contact rule" in very numerous cases, and had found it confirmed in every case where the angle-of-contact in one of the liquids of the emulsion-pair was *consistently* obtuse: in the other cases the same powder could usually be got to stabilise either type of emulsion by suspending it first in the liquid which was to form the external phase, though one type was always more stable than the other. An account of the theory and of these experiments was given at the Liverpool meeting of the British Association for the Advancement of Science in September, 1923.[1] In 1924 it was learned that in June of 1923, Finkle, Draper and Hildebrand[2] had anticipated a small though important part of the above theory, in so far as they had pointed out that the internal phase of an emulsion stabilised by bulk-solid particles would tend to be that in which the contact-angles were obtuse. The experimental evidence brought forward by them in support of the view was the microscopic appearance of emulsions of water-in-benzene stabilised by "lamp-black."

In conclusion, it may be well to add that all the factors concerned in the stabilisation of emulsions by bulk-solid particles must, in Ramsden's opinion, operate in emulsions stabilised by the relatively very small molecules of soluble emulsifiers. For most of the adsorbed molecules actually intersect the adsorption-interface, and the lateral spacings and the levels at which these "interfacial adsorbed molecules," as they may be termed, are intersected by the adsorption-interface, are held to be determined by stresses and free energies which in actions and causation are essentially identical with those which determine the lateral spacings and levels of bulk-solid particles, though they could not be called surface-tensions and there could be no "angle-of-contact" as ordinarily understood. Further, the approximation of two adsorption-surfaces saturated with soluble molecules would be favoured or opposed in ways fundamentally identical with those obtaining when the adsorbed particles were bulk-solids. The problems arising are, however, made much more complex by the fact that the forces exerted between each liquid and the different atoms of the interfacial molecule would usually differ when these atoms were different or differently grouped. For these differences would tend to produce changes of the shape and even of the species of the interfacial molecule, and also to cause its specific orientation, while at the same time the configurations of the two bulk liquids near it would become specifically and complexly modified up to distances often large multiples of z.[1]

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[1] *Nature*, 112, 671 (1923). Cf. Clayton's "Die Theorie der Emulsionen und der Emulgierung" (Berlin, 1924), S. 123.

[2] *Colloid Symposium Monograph*, 1, 205 (1923).

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[1] See Ramsden, *Trans. Faraday Soc.*, **22**, 484 (1926), and Cassel, *J. Phys. Chem.*, **42**, 475 (1938).

CHAPTER VII

DUAL EMULSIONS AND THE INVERSION OF PHASES

WITH two immiscible liquids O and W, it is theoretically possible to obtain two types of emulsion, viz., O dispersed in W and W dispersed in O. Moreover, it would seem at first that one should be able to produce these two sets of emulsions with any given phase ratio, *e.g.*, from 1 per cent. of O in W, or W in O, up to, say, 99 per cent. of O in W, or W in O.

The earlier workers on emulsions all dealt with the familiar type where oil was the dispersed phase, water or an aqueous solution being the dispersing medium. However, it has been shown that water can be dispersed in organic media to form stable emulsions, and various investigators have realised experimentally the theoretical emulsions mentioned above. The subject has much practical application in various industries, *e.g.*, paints, butter and margarine, but its greatest importance lies in its fundamental bearing on the general theory of emulsions and emulsification, and has, in fact, led to the present widely accepted "adsorption-film" theory of emulsions.

As we have already seen (p. 143), Ostwald recognised two types of emulsions, but believed that dual emulsions were restricted within definite phase-volume relationships. He, however, pointed out the significant fact that two emulsions of the same concentration values, but of opposite types, would possess entirely different properties.

The present discussion is concerned not so much with the making of an emulsion of a given type as with the *reversal* of a given emulsion to one of the opposite type.[1]

Robertson[2] was one of the first investigators in this connection, but his work was really an investigation on phase-volume relationships, and as such has already been discussed. The fact that he obtained inversion and two types of emulsion is important; his quantitative results, however, are unsatisfactory.

Newman[3] investigated the two types of emulsion obtained with water and benzene. He found that, using sodium oleate as emulsifier, water was always the external phase, no matter what phase ratio he took. Even 99 c.c. of benzene could be emulsified in 1 c.c. of water containing about 0·05 grm. sodium oleate. This particular emulsion was a stiff jelly. When magnesium oleate was the emulsifying agent employed, Newman obtained emulsions of water in benzene. Newman found that emulsions of water in benzene stabilised by magnesium oleate could be inverted by adding sufficient sodium oleate. Similarly, emulsions of water in carbon disulphide could be inverted.

Briggs and Schmidt[4] extended this work and confirmed Newman's results. Emulsions containing over 90 per cent. of water dispersed in benzene were easily obtained when magnesium oleate was the emulsifying agent. The emulsions of water in benzene, however, are not as stable as those of benzene in water. Barium oleate was not so effective as magnesium oleate.

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[1] See discussion and review by Delbet, *Bull. acad. méd.*, **111**, 907 (1934).

[2] *Kolloid-Z.*, **7**, 7 (1910).

[3] *J. Phys. Chem.*, **18**, 34 (1914).

[4] *Ibid.*, **19**, 478 (1915).

The first thorough study of the actual inversion of an oil-in-water emulsion to one of water-in-oil is due to Clowes, who undertook the work as a result of Bancroft's observation that sodium soaps promote the emulsification of oil in water, whilst calcium soaps promote the reverse type. Similar antagonistic effects are familiar in biology, *e.g.*, the formation of a blood clot from blood plasma, or a casein clot from a casein suspension, both of these processes, as pointed out by Clowes, being promoted by calcium salts and inhibited or retarded by alkalies and sodium salts. As far as physiological systems are concerned, the first to recognise the antagonistic effects of NaCl and $CaCl_2$ therein was Mathews,[1] whilst Clowes first appreciated their influence in emulsion systems, since he showed that an emulsion of oil in water could be changed into one of water in oil by shaking with calcium salts.[2] Shaking again with a sufficient quantity of NaOH would reconvert the emulsion to its original type. Later, Clowes [3] showed that in the case of emulsions of olive oil in water, stabilised by adding NaOH, the addition of $CaCl_2$ can lead to a critical condition where the tendency towards the formation of the two types of emulsions is almost the same. This occurs when equivalent amounts of Ca and OH ions are present, the directive action of the Ca ions being counterbalanced by the action of the OH ions.

He further showed that, in the case of oil-in-water emulsions to which varying amounts of $CaCl_2$ and sodium citrate were added, the antagonistic effects of the calcium and citrate ions disappeared when the two ions were present in the ratio of 1 : 2. A solution of $CaCl_2$ and sodium citrate, in which the ratio of Ca ion to citrate ion is 1 : 2, exerts no influence on the hæmolysis of blood corpuscles, and is inactive when injected intravenously into mice. Solutions where this ion ratio is departed from at once produce positive effects. Clowes tentatively suggested that the activity of the ions was resultant upon adsorption.

INVESTIGATIONS BY CLOWES

In an exhaustive paper entitled "Protoplasmic Equilibrium," Clowes,[4] in 1916, gave a detailed discussion on the inversion of emulsions. At the outset he insisted that in the inverting action of $CaCl_2$ on emulsions of oil in very dilute NaOH there is no antagonistic action between the cations Ca and Na, but rather between cations and anions adsorbed on or reacting with the surface films or enveloping membranes which surround the dispersed globules in a stable emulsion. "It simply happens that, in the case of $CaCl_2$, the cation Ca is far more readily adsorbed than the anion Cl, while in the case of NaCl, the anion Cl is somewhat more readily adsorbed than the cation Na."

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[1] *Am. Journ. Physiol.*, **11**, 455 (1904).

[2] *Proc. Soc. Exp. Biol. and Med.*, **11**, 1 (1913).

[3] *Kolloid-Z.*, **15**, 123 (1914).

[4] *J. Phys. Chem.*, **20**, 407 (1916). See also Seelich, *Kolloid-Z.*, **85**, 268 (1938). A comprehensive account of the work of Fernbacher, *Inaug. Diss.* (Greifswald, 1932), is given by Degkwitz in "Lipoide und Ionen" (Dresden, 1933), p. 185.

The emulsions contained equal volumes of water and olive oil, the latter containing sufficient free oleic acid to form soap with all the added NaOH. Shaking was carried out by a mechanical shaker, followed by hand shaking. The effect of carrying proportions of NaOH and $CaCl_2$ on such an emulsion containing 10 c.c. each of oil gave results which showed that when the ratio of NaOH to $CaCl_2$ is exactly 4 : 1, neither type of emulsion predominates. Oil-in-water emulsions result when this ratio is greater than 4 : 1, and water-in-oil emulsions when the ratio is less than 4 : 1. At the critical point one chemical equivalent of $CaCl_2$ is always present with two of NaOH, so that sodium oleate and calcium oleate are present in equivalent proportions. The type of emulsion, therefore, depends on the nature of the soap present, sodium oleate leading to dispersion of water in oil. The theoretical explanation of this has been advanced by Bancroft and accepted by Clowes, and is dealt with in the following chapter.

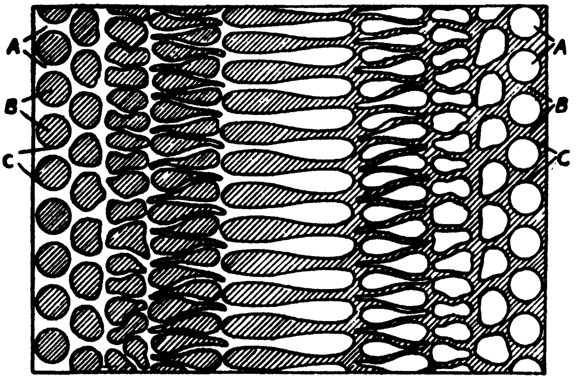

FIG. 41. Inversion of emulsions (Clowes).
A = water; B = oil; C = adsorbed film.

Clowes followed the actual inversion of an oil-in-water emulsion by means of the microscope. The oil globules become distorted, and near the critical point become elongated. At this stage the Brownian movement is very prominent. At the critical point larger masses of oil and water are in very active movement, probably owing to the existence of two continuous phases. When the critical point is passed, the emulsion mainly contains large drops of water surrounded by oil. In the water drops there are still small globules of oil exhibiting rapid Brownian movement; conversion to the water-in-oil emulsion is regarded as complete when this particular Brownian movement entirely ceases. A schematic presentation of such inversion is given by Clowes, and reproduced in Fig. 41.

Parsons and Wilson [1] have also described the behaviour of emulsions when undergoing inversion. Using emulsions of "Nujol" (mineral oil) in dilute sodium oleate solutions and adding magnesium salts, inversion was obtained. The first effect of adding a Mg salt was greatly to lower the viscosity of the oil-in-water emulsion. This was followed by an increase in viscosity, with oil appearing as the external phase. The explanation advanced for these effects is that the Mg salt reacted with the sodium soap in the adsorbed film, and caused a temporary breaking of the emulsion. The magnesium oleate produced by metathesis then dissolved in the oil, promoting an emulsion of water in oil, a system of the viscosity characteristic of emulsions.

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[1] *Ind. Eng. Chem.*, **13**, 1119 (1921).

Other electrolytes were investigated, and it was found that salts of Mg, Sr. Ba, Fe, Al, etc., exerted a comparable effect to Ca, whilst in place of NaOH could be used KOH, LiOH, etc. With $MgCl_2$ and NaOH a critical ratio appears when the proportions of Na oleate and Mg oleate are equivalent. Clowes classified electrolytes into two main groups: (1) promoting dispersion of oil in water—salts of the monovalent Li, Na, K, etc., alkalies, salts of di- and trivalent anions; (2) promoting dispersion of water in oil—salts of the di- and trivalent cations Ca, Sr, Ba, Fe, Al.

Employing a Traube stalagmometer, Clowes determined the number of drops obtained when a given volume of solutions of electrolytes was run into olive oil containing "a certain amount of oleic acid." The principle involved is that underlying the Donnan pipette, namely, that the greater the number of drops obtained, the more pronounced is the tendency to produce emulsification.

Clowes found that NaCl and KCl in small amounts promoted the formation of emulsions of oil in water, and counteracted the effect of $CaCl_2$ in the approximate ratios of 100 to 150 molecules of NaCl to one of $CaCl_2$.

The following table of drop-numbers is given by Clowes, and shows the opposing influences of NaCl and $CaCl_2$:—

TABLE 30

Na˙—Ca˙˙ ANTAGONISM IN EMULSIONS

Experiment.	Concentration of			Drop-number.	Mol. ratio NaCl : $CaCl_2$.
	NaOH.	NaCl.	$CaCl_2$.		
1	0·001 M	—	—	44	—
2	,,	0·15 M	—	300	—
3	,,	—	0·0015 M	24	—
4	,,	0·15 M	0·0015 M	44	100 : 1
5	,,	0·3 M	0·003 M	43	100 : 1
6	,,	0·45 M	0·005 M	43	100 : 1·1
7	,,	0·6 M	0·01 M	43	100 : 1·6

The dispersing influence of NaCl is well illustrated in Experiment 2, and the opposite effect of $CaCl_2$ in Experiment 3. When the NaCl and $CaCl_2$ are in such amounts as to correspond to the ratio of about 100 molecules NaCl to one molecule of $CaCl_2$, the drop-number attains the same value as the original number obtained with NaOH alone, thus showing that the opposing effects of NaCl and $CaCl_2$ are counterbalanced.

Clowes argues that the antagonistic effects of various electrolytes on emulsions and biological systems may be used to classify electrolytes into two main groups: (1) those possessing a relatively more readily adsorbed or reactive cation than anion, and (2) those possessing a relatively more readily adsorbed or reactive anion than cation. "Balanced solutions are those in which the relative proportions of cations and anions reacting with or adsorbed by colloidal constituents of the surface film are such that no change occurs in the charge in the state of dispersion, and consequently in the permeability of the film."

Clowes summarises his own work in the statement that emulsion equilibrium depends on the relative proportion of positive and negative ions adsorbed by the stabilising film around the dispersed globules; when negative ions are in excess, the oil-in-water type of emulsion is favoured, whilst an excess of positive ions has the reverse effect. This idea has been favoured by Bhatnagar, who, however, has pointed out its limitations and shown how it should be extended.

The idea that adsorption of ions is the underlying factor in emulsion equilibrium is supported by experiments of Clowes, wherein he shows that the ratio between the number of drops obtained when varying concentrations of sodium oleate solutions flow into oil and the concentration of the soap is always logarithmic. Also, when electrolytes like NaOH or $CaCl_2$ are added, the ratio between the number of drops and the concentration of the electrolyte is again logarithmic. In support of this, too, is the fact that a logarithmic relationship holds for the ratio of concentration of added NaCl, and the concentration of the OH ions in the aqueous phase, when NaCl is added to an emulsion of oil in water.

INVESTIGATIONS BY BHATNAGAR

Bhatnagar has made considerable investigation into the inversion of emulsions by electrolytes, employing the electrical method suggested by Clayton[1] as a sensitive means of detecting the inversion point. His first experiments[2] were with emulsions of paraffin oil (B.P.) and water in equal volumes, the oil containing 1 per cent. of oleic, stearic, or linoleic acid. The oil was shaken in a mechanical shaker with the water, to which varying proportions of KOH and electrolytes had previously been added. The reversing effect of barium nitrate on an emulsion of paraffin oil containing 1 per cent. oleic acid and varying amounts of KOH is shown as follows: (The volume of oil was 10 c.c., and the volume of the aqueous phase was maintained throughout at 10 c.c.).

Vol. M/50 KOH c.c.	Vol. M/50 $Ba(NO_3)_2$ c.c.						
	0·2	0·4	0·6	0·8	1·0	1·2	1·4
1	R	W—O	W—O	W—O	W—O	W—O	W—O
2	O—W	R	W—O	W—O	W—O	W—O	W—O
3	O—W	O—W	R	W—O	W—O	W—O	W—O
4	O—W	O—W	O—W	R	W—O	W—O	W—O
5	O—W	O—W	O—W	O—W	R	W—O	W—O
6	O—W	O—W	O—W	O—W	O—W	R	W—O

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[1] *Brit. Assocn. Colloid Reports*, **2**, 114 (1918).

[2] Bhatnagar, *J. Chem. Soc.*, **117**, 549 (1920); *vide* criticism by Bancroft, *Ind. Eng. Chem.*, **13**, 348 (1921).

Just as Clowes found that the critical point with emulsions of oil and water containing NaOH and $CaCl_2$ was 4 molecules of NaOH to 1 molecule of $CaCl_2$, so Bhatnagar found that at the critical point the ratio of KOH to $Ba(NO_3)_2$ was 4 : 1 in concentrations ranging from M/10 KOH upwards. In lower concentrations the ratio increases; thus at M/50 KOH it is about 5 : 1. He also found that the nature of the acid in the oil influenced the critical ratio. Thus, when using KOH and $Ba(NO_3)_2$ in M/10 concentration, but replacing oleic acid with linoleic acid, the critical point was reached when the ratio of KOH to $Ba(NO_3)_2$ was 2 : 1.

Bhatnagar,[1] recognising that the presence of free alkali and free fatty acid makes the system more complex, investigated the inversion of paraffin oil (B.P.) emulsions stabilised by various *soaps*. The emulsions were made up as before, and in all cases contained 10 c.c. each of oil and the aqueous phase. Each emulsion contained a known amount of a definite soap and known quantities of various electrolytes. The results are given in the following table, and are expressed in millimols per cent. of the electrolytes at the critical (inversion) point.[2]

TABLE 31

INVERSION OF EMULSIONS BY ELECTROLYTES

Emulsifying Agent.	Amount of Soap in Millimols per cent.	Electrolytes in Millimols per cent. at Inversion Point.					
		$Ba(No_3)_2$.	$Sr(NO_3)_2$.	$Pb(NO_3)_2$.	$Ni(NO_3)_2$.	$Al_2(SO_4)_3$.	$Cr_2(SO_4)_3$.
Na. Oleate . .	0·080	0·0398	0·0398	0·0396	0·036	0·014	0·016
	0·101	0·0500	0·052	0·504	0·040	0·017	0·019
	0·150	0·080	0·084	0·082	0·060	0·025	0·027
	0·162	0·084	0·090	0·088	0·076	0·027	0·030
	0·210	0·112	0·116	0·110	0·0798	0·036	0·039
K. Stearate .	0·086	0·044	0·046	0·040	0·040	0·018	0·018
	0·10	0·0508	0·0512	0·050	0·052	0·026	0·022
	0·15	0·084	0·086	0·078	0·088	0·027	0·026
	0·25	0·132	0·136	0·128	0·140	0·048	0·048
	0·30	0·156	0·160	0·150	0·154	0·056	0·057
Li. Stearate.	0·09	0·040	0·040	0·036	0·042	0·015	0·016
	0·12	0·058	0·058	0·050	0·056	0·021	0·023
	0·16	0·090	0·094	0·080	0·094	0·028	0·029
	0·20	0·102	0·104	0·096	0·106	0·03	0·032
Na. Linoleate	0·088	0·068	0·068	0·058	0·072	0·028	0·028
	0·112	0·100	0·106	0·090	0·116	0·038	0·037
	0·125	0·128	0·134	0·120	0·136	0·042	0·043
	0·18	0·198	0·200	0·178	0·200	0·061	0·063

A study of the above results brings out several well-marked features: (*a*) There is a distinct valency effect of the electrolyte. Trivalent electrolytes, the sulphates of aluminium and chromium, are required in much smaller amounts to effect inversion of the oil-in-water emulsions than are the bivalent electrolytes. (*b*) The inverting capacity of the electrolytes follows the order Al > Cr > Ni > Pb > Ba > Sr (calcium, bivalent iron and magnesium possess the same values as strontium). (*c*) The nature of the soap present influences the amount of electrolytes required to effect the reversal of phases, but the valency effect of the electrolyte still appears.

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[1] *J. Chem. Soc.*, **119**, 61 (1921).

[2] *Loc. cit.*, p. 63, where "respective salts in millimols at R" should read "respective salts and soaps in millimols per cent. at R."

Bhatnagar[1] observed the effect of altering the volume ratio of the phases in emulsions with different soaps and the same series of multivalent electrolytes. In all cases it was found that the amount of electrolyte necessary to effect the reversal of phases increased as the volume of the aqueous phase was increased, and diminished as it was reduced. A corresponding increase in the oil phase had the opposite effect. Thus in one case where barium nitrate was added to an emulsion of oil and water containing lithium stearate, and in which the total volume of emulsion was kept at 20 c.c., the following results were obtained :—

Ratio $\frac{\text{Vol. of Aquecus Phase}}{\text{Vol. of Oil Phase}}$.	Ratio $\frac{\text{Mols. of Lithium Stearate at R}}{\text{Mols. of Barium Nitrate at R}}$.
1·00	4·13
3·00	3·43
0·33	6·00

The effect of free fatty acids and alkalies on emulsion equilibrium has been found by Bhatnagar to result in a shift of the inversion point. Three sets of emulsions of the same sodium oleate content, viz., 0·162 millimols per cent., and of the same volume ratio were taken. In one the oil contained free fatty acid, in the second free alkali was present in the aqueous phase, whilst the third contained neutral oil and the soap solution. Barium nitrate was the electrolyte used, and the data given below express the concentration of $Ba(NO_3)_2$ at the inversion point :—

Vol. Emulsion.	Free KOH.	Free Fatty Acid.	$Ba(NO_3)_2$.
c.c.	grm.	grm.	Millimols per cent.
20	0·01	*Nil.*	0·09
20	0·021	*Nil.*	0·096
20	*Nil.*	0·003	0·078
20	*Nil.*	0·008	0·070
20	*Nil.*	*Nil.*	0·084

Apparently, free fatty acids and free alkalies shift the inversion point in opposite directions.

Parsons and Wilson[2] have studied the inversion of oil-in-water emulsions, using the highly-purified mineral oil known as "Nujol." The emulsions were passed five times through a Briggs' homogeniser,[3] and the oil phase and water phase were of equal volume. The effect of the presence of opposing emulsifying agents was investigated, sodium oleate being dissolved in the water phase and magnesium oleate in the "Nujol." Numerous emulsions were made, varying the ratio of equivalent concentration of magnesium oleate to sodium oleate from 25 to 0·54. The existence of real equilibrium in the presence of these opposing emulsifiers was looked for, as well as the existence of a possible critical ratio of the reagents at which no emulsion at all would result. The general results of the work showed that a pure mineral oil behaves differently to an oil such as olive oil (as used by Clowes), since no critical ratio of magnesium oleate to sodium oleate was observed, at which inversion to a new stable emulsion would occur. Some sort of pseudo-equilibrium was reached whereby *both* types of emulsion would co-exist. This is an important point.

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[1] *Loc. cit.*
[2] *Ind. Eng. Chem.*, **13**, 1116 (1921).
[3] *J. Phys. Chem.*, **19**, 223 (1915).

Parsons and Wilson tried the inverting effects of various di- and trivalent salts on Nujol-in-water emulsions stabilised with sodium oleate. Aqueous solutions of $MgSO_4$, $MgCl_2$, $FeSO_4$, $Al_2(SO_4)_3$ and $FeCl_3$ were used. The volume ratio of oil to total emulsion in the resulting mixture was maintained at 0·5.

With the magnesium salts no absolutely sharp inversion point was found, but rather a time period of instability during which inversion took place. When the equivalent concentration of magnesium exceeded that of sodium, the original oil-in-water emulsion was completely inverted to one of water-in-oil. Both types of emulsion resulted from the equivalent concentration of magnesium approached, but did not exceed, that of sodium. The important point was noted that the determining factor in the inversion of these emulsions was the ratio of *equivalents* of magnesium to sodium, not the absolute concentrations. Variations in the *anion* of the added electrolyte had but little effect on the emulsion equilibrium.

When ferrous sulphate solution was added to Nujol-in-water emulsions, inversion occurred when the ratio of the equivalent concentration of ferrous sulphate to sodium oleate exceeded 1. The new emulsion soon broke down, since the iron soap possesses a weak emulsifying tendency.

No quantitative results are given for the effects of the trivalent electrolytes. Complete inversions took place, but the water-in-oil emulsions were very unstable, pointing to the very weak emulsifying tendencies of the aluminium and iron soaps.

REVERSAL BY ELECTROLYTES

Bhatnagar [1] has published a valuable paper on the reversal of emulsion type by electrolytes. These emulsions, too, were of a mineral oil (B.P. paraffin oil), but the emulsifying agents included insoluble suspensions specially prepared and purified, viz., zinc hydroxide, lead oxide, lead carbonate, casein, lecithin, egg albumin, and rosin. The zinc hydroxide was obtained by adding KOH to a 3 per cent. solution of pure $ZnSO_4$ until the precipitated hydroxide redissolved. Dilute HCl was then cautiously added until the precipitate just reappeared. The coagulum and liquor were dialysed in parchment for five days, when the diffusion of alkali ceased and a wash-liquid neutral to litmus resulted. The coagulum was then made up to 1 litre. It was capable of maintaining stable emulsions of paraffin oil and water, the alkali-free suspensions of zinc hydroxide promoting the water-in-oil type of emulsion, whilst alkaline suspensions of zinc hydroxide promoted the reverse type. Dried zinc hydroxide was not able to stabilise emulsions at all. This may be due to the film of adsorbed air which prevents the wetting of dried powders.[1]

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[1] *J. Chem. Soc.*, **119**, 1760 (1921).

In the discussion of his results Bhatnagar mentions that lecithin and egg albumin promote the oil-in-water type of emulsions. The addition of a small quantity of KOH, K_3PO_4 or Na_2CO_3 to the aqueous phase increases the stability of such emulsions, whilst addition of sufficient acid inverts the emulsions to the unstable water-in-oil type. A zone of instability precedes the inversion, and this zone is clearly seen in most cases, especially when sufficient emulsifying agent is present.

Bhatnagar formulates two empirical rules which hold for his results: (1) "An emulsion of water in oil can be transformed into one of oil in water by electrolytes having reactive anions like OH' and PO_4'''. (2) An emulsion of oil in water can be transformed into the reverse type by electrolytes having reactive cations like $H^{\cdot}$, $Al^{\cdot}$, $Fe^{\cdot\cdot\cdot}$ and $Th^{\cdot\cdot\cdot\cdot}$."

Clowes [2] deduced a similar classification of what he termed "antagonistic electrolytes" into two groups: "The first consists of di- and trivalent cations, etc., which possess a more readily adsorbed cation and promote the formation of the emulsion of water in oil; the second consists of alkalies, salts of monovalent cations, and of di- and trivalent anions which possess a more reactive and more readily adsorbed anion, and appear to exert the reverse effect of promoting the formation of oil dispersed in water."

Summarising his own work, Bhatnagar gives the following table dealing with emulsion reversal:—

TABLE 32

BHATNAGAR'S DATA ON EMULSION REVERSAL

Emulsifying Agent.	Reversing Electrolyte. Salts of :—	Emulsion Type.	Adsorbed Ions. Excess of :—
Sodium oleate	Ba, Ca, Sr, Fe, Cr	O/W	+ ions.
	Al, Cu, Zn, Ni	O/W	+ „
Carbon	KOH, K_3PO_4	W/O	− „
Casein	Al, Fe, Th, H	O/W	+ „
Albumin	—	—	+ „
$Zn(OH)_2$ neutral	KOH, K_3PO_4	W/O	− „
$Zn(OH)_2$ alkaline	Al, Th, H	O/W	+ „
$Al(OH)_3$	KOH, K_3PO_4	W/O	− „
PbO	KOH	W/O	− „
Rosin	KOH, K_3PO_4	W/O	− „
Lecithin	Al, Fe, Th	O/W	+ „
Univalent soaps	Bivalent and trivalent metals	O/W	+ „

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[1] Cf. Ehrenberg and Schultze, *Kolloid-Z.*, **15**, 183 (1914).

[2] *J. Phys. Chem.*, 20, 449 (1915); cf. Hirschfelder and Serles, *J. Pharmacol. Exp. Therap.*, 29, 441 (1926).

KING AND WRZESZINSKI'S RESULTS

Pointing out that certain new synthetic emulsifying agents promote stable emulsions which are unaffected by considerable additions of electrolytes, King and Wrzeszinski [1] argued that according to the chemical theory of phase inversion, this inertness would be explained by the absence of insoluble salts with polyvalent cations, but the physical theory would demand inversion by electrolytes under certain conditions. They decided to re-examine the whole question of the influence of electrolytes on emulsions and their first paper contains data as to the effect of various salts on emulsions stabilised by agents which do not form insoluble salts with heavy metals, including some of the agents examined by Bhatnagar and also two " Daxads " (polymerised organic salts of sulphonic acids of the alkyl-aryl type). Distilled water and kerosene were the two liquids chosen.

Table 33 is reproduced from their report. Their general conclusion is that where the emulsifying agent cannot form a water-insoluble salt with polyvalent metals, electrolytes have little influence on the type or stability of emulsion, except when there occurs some chemical change destructive of the emulsifying action.

TABLE 33

Emulsifying Agent.	Dispersion Medium and Concentration (Per Cent.) of Agent.	Type of Emulsion.	Effects of Electrolytes.
Gum dammar	1·00 in oil	W/O and [O/W]	Emulsion broken by NaOH and NH_4OH stable towards Na_2HPO_4 and cations (H^+, Al^{+++}, Th^{++++}).
Carbon black	1·00 in oil	W/O	No reversal or breaking.
Agar agar .	1·00 in water	O/W	,,
Lecithin .	1·00 in water	O/W	,,
Bentonite .	1·00 in water	O/W	,,
Egg yolk .	1·00 in water	O/W	,,
Saponin .	1·00 in water	O/W and [W/O]	,,
Gum acacia .	1·00 in water	O/W and [W/O]	,,
Daxad 21 .	1·00 in water	O/W	,,
Daxad 27 .	1·00 in water	O/W	,,
$Zn(OH)_2$.	0·317 in water	O/W	Broken by HCl and Al^{+++}, stable to Th^{++++} although particle size was increased.
$Al(OH)_3$.	0·412 in water	O/W	Stable to salt anions and cations, also H^+ and OH^- broken only by conc. acid or alkali.

Square brackets indicate that the emulsion type enclosed was very unstable and tended to revert to the more stable type on shaking. The existence of both emulsion types with a given system is in line with the observations of Cheesman and King.[2]

" It is generally assumed that O/W emulsion particles are negatively charged while those of W/O type are positive. If this is so, the physical theory would lead us to expect O/W emulsion to be inverted by the addition of Al^{+++} or Th^{++++}, while phase reversal of W/O emulsions should be brought about by the addition of OH^- or PO_4^{---}. This has not been observed in the present work which thus lends strong support to the chemical theory. With the solid hydroxides, excess of acid or alkali destroyed the emulsion, but this was obviously due to solution of the agent at the interface. With emulsions stabilised by gum dammar alkalis caused breakage but not inversion ; it seems not unlikely that this again is due to a chemical rather than a physical action of the alkali on the gum.

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[1] *Trans. Faraday Soc.*, 35, 741 (1939).

[2] *Ibid.*, 34, 594 (1938).

Emulsions stabilised with carbon black, although unaffected by electrolytes underwent a considerable increase in viscosity on the addition of alkali ; a similar effect was noted with bentonite stabilised emulsions on the addition of acid, aluminium or thorium salts and with the daxad emulsions in the presence of aluminium salts. Increased foaming was caused by the addition of the electrolytes to emulsions stabilised with agar agar, gum acacia, egg yolk and the daxad reagents.

" Zinc and aluminium hydroxides for use as emulsifying agents were prepared by the action of dilute ammonia on solutions of salts of these metals. The gelatinous precipitate was washed and then dialysed until quite free from alkali. Even under the most favourable conditions it was found possible to prepare only O/W emulsions and not the W/O type reported by Bhatnagar."

INVERSION IN THE PRESENCE OF SOAPS

The question of emulsion reversion in the presence of soaps has received very considerable attention within the last few years, and the explanations of Clowes and Bhatnagar have been shown to require revision. Thus it has been pointed out [1] that Bhatnagar overlooked the fact that a stoichiometric relationship existed in some of his results, the amount of electrolyte needed to invert an emulsion closely approximating the amount needed to convert sodium oleate to the corresponding soap of the di- or trivalent cation. " It must be admitted, however, that this simple relationship does not apply when sodium linoleate was the emulsifying agent nor does it explain why more multivalent electrolyte is required to bring about reversal of phase when the external phase is diluted without changing the absolute amount of sodium oleate present."

Tartar and his associates [2] showed for the first time that the type of emulsion could be changed by the use of univalent electrolytes yielding the *same* cation as the soap. Emulsions of benzene, toluene, or xylene with water and sodium oleate, exhibited a well-defined zone of instability between NaCl concentrations of 0·25 N to 0·45 N with benzene ; the inversion point was somewhat displaced as the concentration of NaOH was raised, although no such pronounced effect was obtained with toluene or xylene. Significant to note, all the emulsions produced by the aid of potassium stearate were O/W systems and no inversions could be effected by the addition of KCl and KOH.

Later, Tartar and others [3] reported that NaCl inverted emulsions of water with benzene, xylene, chloroform or carbon tetrachloride when the less soluble sodium soaps, the oleate and stearate, were employed as emulsifying agents. No inversion resulted when the more soluble sodium laurate was used. Further, attempts to invert emulsions stabilised with potassium stearate, oleate, laurate, and pelargonate (characterised by greater solubility than possessed by the corresponding sodium soaps) by the addition of KCl failed ; always O/W systems obtained.

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[1] Tartar *et al.*, *J. Phys. Chem.*, **33**, 437 (1929).

[2] *Ibid.*, **33**, 435 (1929).

[3] *Ibid.*, **34**, 373 (1930).

PHASE-PARTITION OF SOAPS

Highly important observations were next reported by Wellman and Tartar [1] relating to the transfer of soap from the aqueous phase of the organic liquid phase. With such liquids as C_6H_6, C_6H_5–CH_3, CCl_4 and gasolene, contact with concentrated solutions of the higher saturated sodium soaps in water led to a transfer of soap across the dineric interface. The organic liquid received soap to an amount depending on the original concentration of soap and the organic liquid used. The authors stated : "This transfer phenomenon has been observed with thirteen liquids, immiscible with water ; there are, no doubt, many more which will display similar behaviour. The writers believe that this *important property of certain soaps has been entirely overlooked in the study of emulsions.*" The distribution of the soap between the phases, irrespective of the metal involved, is emphasised as a hitherto ignored type-determining factor.

Previous work had shown that the inversion point of soap emulsions is influenced by changes of temperature ; rise in temperature favoured the O/W and lower temperature the W/O type respectively. The present research confirmed this. Emulsions were prepared by adding 5 c.c. of benzene to 5 c.c. of hot soap solution and cooled to 5° C. Examination for type was made at intervals of rising temperature of 2·5° C., until emulsions of all soap concentrations had inverted. Fig. 42, reproduced from Wellman and Tartar's paper, shows interesting conclusions. "To the left and above the temperature-concentration curves the corresponding soap was unable to stabilise W/O emulsions, whereas the area indicated under the curves produced only that type. The greater solubility of sodium palmitate over stearate in water is reflected in its lower 'limiting temperature of inversion' at which the curves become approximately horizontal. These limiting temperatures are within a few degrees of the temperatures at which the soap solutions themselves lose their macroscopic colloidal appearance and apparently become clear solutions. The sharpness of this change is quite noticeable, for most of the suspended soap disappears at once."

The authors next dealt with emulsions stabilised with bivalent soaps. Again, it was found that an important factor in determining emulsion type is the distribution of bivalent soaps between the phases. Oil-in-water emulsions resulted when dilute aqueous solutions of Mg heptylate, caprylate or caproate, or Ca valerate were shaken with equal volumes of benzene. Using more concentrated solutions of the bivalent soaps, in which solid or colloidal soap was present, promoted W/O emulsions, very unstable, the soap being largely precipitated in the non-aqueous phase. Whilst the addition of further benzene favoured the W/O systems, small amounts of water caused inversion on shaking.

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[1] *Ibid.*, **34**, 379 (1930).

Such qualitative observations supported the belief that "increasing the relative amount of soap in one of the phases tends to make that phase the dispersion medium of the emulsion." Increasing the volume of such a phase (thus altering the concentration of soap in the opposite phase) or causing a temperature change favouring the transfer of the soap to that phase, may accomplish this.

Since dry benzene solutions of soaps are clear, and contact with water precipitates soap, doubt is obviously thrown on the assumption that the reason for inversion from O/W to W/O type is due to solubility of the bivalent soap in benzene. "There is no doubt, however, that the precipitated or flocculent bivalent soap is more easily wetted by benzene than by water." The instability of W/O emulsions is related to the fairly inelastic, solid films, or films of little cohesive strength, affected, too, by the presence of electrolytes. A new observation was that O/W emulsions could be prepared by the aid of Ca, Mg and Ba oleates, which are sufficiently soluble in water. Whilst such emulsions in the absence of electrolyte persisted for an hour, their life in the presence of NaCl, $BaCl_2$, $CaCl_2$ or $MgCl_2$ was quite short. This is attributed to the action of the electrolyte on the flocculent soap in the interface.

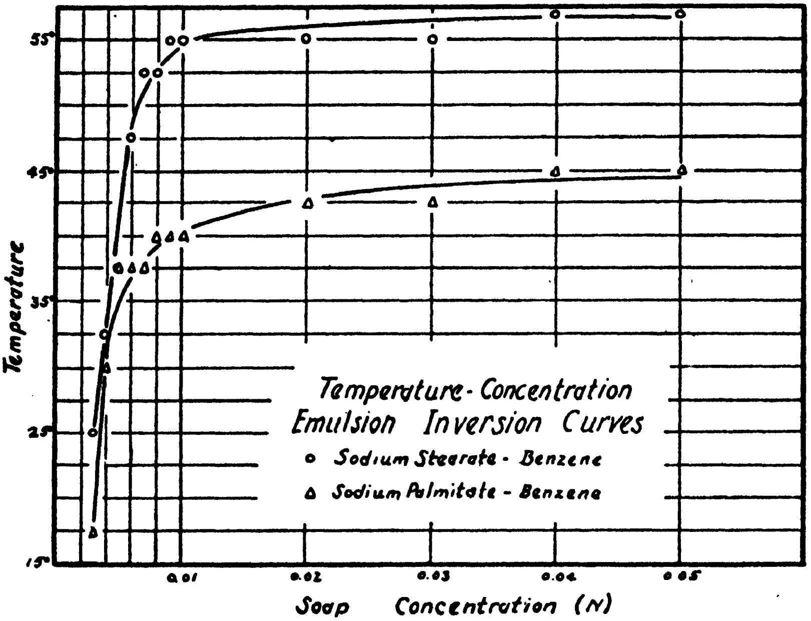

FIG. 42. Influence of temperature and concentration of soap upon the inversion of emulsions (Wellman and Tartar).

Wellman and Tartar followed now with a series of experiments on the effects of NaCl and $CaCl_2$ on emulsions of C_6H_6 in aqueous sodium oleate at 25° C., in order to test Clowes' views that the opposing influences of these two electrolytes are related to the preferential adsorption of ions by the soap films. The authors point out that Clowes' "emulsion equilibrium" for systems containing both NaCl and $CaCl_2$ should obtain by the addition of either salt to emulsions containing the other; moreover, the Clowes' ratio of 100 molecules of NaCl to 1 molecule of $CaCl_2$, if due to an ion-adsorption equilibrium, should be exhibited in any emulsion containing sodium oleate, NaCl and $CaCl_2$.

However, addition of $CaCl_2$ to the benzene emulsions containing NaCl showed that the presence of NaCl had no appreciable influence on the inverting action of $CaCl_2$. The data in Table 34 are taken from the authors' paper.

TABLE 34

EFFECTS OF NACL AND $CACL_2$ ON EMULSIONS OF BENZENE IN AQUEOUS SODIUM OLEATE (0·01 N) AT 25° C.

NaCl.	$CaCl_2$ (Normality).						
	0·0.	0·0001.	0·001.	0·005.	0·006–0·009.	0·01.	0·0125.
0·0	O/W	O/W	O/W	O/W$_x$	O/W	W/O	W/O
0·05N	O/W	O/W	O/W	O/W$_x$	O/W	W/O	W/O
0·10N	O/W	O/W	O/W	O/W	O/W	W/O$_z$	W/O
0·15N	O/W	O/W	O/W	O/W	O/W	W/O$_z$	W/O

Emphasis must be laid on the importance of the equivalent concentrations of sodium oleate and $CaCl_2$ at the inversion points. According to Clowes' 100 : 1 molecular ratio, the O/W emulsions should have broken at the concentrations marked (x) and an inversion should have been effected at the concentrations marked (z). Again, if Na and Ca oleates possess equal but opposite emulsifying powers, no emulsion should have obtained with 0·005 $NCaCl_2$ in the absence of NaCl, since the soaps were then in equivalent proportions.

The W/O emulsions separated on standing for less than 30 minutes into two layers and at the interface the considerable soap precipitated pointed to an *additive* rather than *antagonistic* effect of NaCl to $CaCl_2$. Such additive action was exhibited to even more marked extent when the emulsions contained carbon tetrachloride instead of benzene. Evidence was also obtained of a slight additive effect of KCl to $BaCl_2$ on emulsions of benzene in aqueous K oleate.

Wellman and Tartar conclude that their experiments contradict the generality of Clowes' "emulsion equilibrium," and the explanation of his phenomenon lies in the uncertainties of his complicated emulsions. "The instability of the systems reported here as the equivalent concentration of $CaCl_2$ approaches that of sodium oleate, and the breaking and inverting of the systems when these concentrations become equal, regardless of the presence of NaCl, demonstrate that the complete conversion of the water-soluble soap present to one much less soluble in water is the underlying cause of the breaking and inverting of these emulsions." Thus, the investigations confirm the results of Parsons and

Wilson (see p. 230) who showed that in the inversion of O/W emulsions, stabilised by sodium oleate, by Mg salts, the determining factor was the ratio of the *equivalents* of Mg to Na. Instead of Clowes' rendering: ions *adsorbed on*, Wellman and Tartar would have *reacting with the soaps* as the true inversion agents.

IMPORTANCE OF SOAP CONCENTRATION

A series of important papers has been published by Weichherz. The first[1] deals with the influence of the soap content of the two phases on the kind of emulsion obtained. Higher concentrations of soap promote W/O emulsions and lower concentrations of soap O/W emulsions. Thus, Table 35 from his paper :—

TABLE 35

INFLUENCE OF SOAP CONCENTRATION OF PARAFFIN/WATER EMULSION

Soap Content (calculated on Paraffin Oil).	Aqueous Phase (in per cent. of the Oil Phase).									
	1	2	3	4	5	8	10	12	15	20
Per cent.										
0·1	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W
0·5	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W
1·0	W/O	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W	O/W
3·0	W/O	W/O	W/O	O/W	O/W	O/W	O/W	O/W	O/W	O/W
5·0	W/O	W/O	W/O	W/O	W/O	W/O	O/W	O/W	O/W	O/W
8·0	W/O	W/O	W/O	W/O	W/O	W/O	W/O	W/O	O/W	O/W

It will be noted that the critical point varies as the soap content varies. Dilution of a W/O emulsion with water leads to a critical phase-volume ratio and inversion to O/W emulsion. The critical point possesses no stereometric significance ; really, a critical soap concentration is involved.[2]

There is a partition of the soap between the two phases. What matters is the relative difference in the wettability of the interfacial layer of soap (molecules or micelles) or, rather, soap + solvent complexes.

In later papers, Weichherz[3] deals with the system : xylol/phenol/sodium oleate/water. He chose an arbitrary ratio of the first three components, 79·94, 12·91 and 7·15 per cent., and added varying amounts of water. From 0–4·66 per cent. of water, a true solution results. Two phases exist between 4·66–21·9 per cent. of water, after which a second homogeneous region up to 24·9 per cent. exists. Two phases again appear, persisting up to 100 per cent. of water. The first heterogeneous mixture is a W/O and the second an O/W emulsion. (Photomicrographs illustrating these conditions are given by Weichherz[4] and corresponding viscosity data by Weichherz and Saechtling.)[5]

Temperature alterations caused shifts of all the regional limits.

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[1] *Kolloid-Z.*, **47**, 133 (1929).

[2] See Auerbach, *Kolloid-Z.*, **51**, 176 (1930) on blubber oil emulsions with soda.

[3] *Kolloid-Z.*, **49**, 158 (1929) ; **74**, 330 (1936).

[4] *Ibid.*, **58**, 214 (1932).

[5] *Ibid.*, **60**, 192, 298 (1932). See also Angelescu and Popescu, *ibid.*, **51**, 336 (1930), and Bailey, *J. Chem. Soc.*, **123**, 2579 (1923) on the system : soap/cresol/water.

Raising the temperature caused displacement of all the regional limits in the direction of lesser quantities of water ; thus, the first homogeneous region and that of W/O emulsions became more narrow, whilst the second homogeneous region and that of O/W emulsions became more extended.

The results were discussed on the basis of the adsorption and degree of solvation of soap in the interface. The orientation of the soap depends on the nature of the ' shell ' of solvent. The greater the hydration of the soap, the less is the stability of W/O emulsions. At a critical ratio of hydrated and non-hydrated soaps, the emulsion is destroyed. Further hydration leads to O/W emulsions.

Related experiments have been reported by Bird[1] in a study of "aqueous dry-cleaning soaps." Investigating the system : potassium oleate/water/white spirit, Bird found that the amounts of water required for solution and inversion are almost directly proportional to the amounts of potassium oleate present, and the amount of water required for inversion is about double the amount required for solution.

SOLVENT PROPERTIES OF SOAPS

Under the title : " Some Solvent Properties of Soap Solutions," Lester Smith[2] has thrown considerable light on the problems connected with soaps as emulsifying agents.

Firstly, a study was made of the solubility of organic liquids in a 0·4 N_W sodium oleate solution at 20° C. In addition, an emulsion of equal parts of the organic liquid and the saturated soap solution was prepared and the stability noted. Taking as an arbitrary dividing line a solubility of about 2 per cent. in water, it was found that with few exceptions the liquids only slightly soluble in water are soluble in the soap solution to a concentration up to 10 per cent. ; usually they increase the viscosity of the solution and yield stable O/W emulsions. In contrast, those liquids more soluble in water show a solubility in the soap solution of 10 per cent. or more, frequently decreasing its viscosity and yielding unstable O/W emulsions.

The author furnishes a list of 32 organic liquids so classified, and his table shows " that every substance which cannot be emulsified permanently by the soap solution is paralleled by another of the same class, often a homologue, which can be emulsified. The converse is, however, not true ; no hydrocarbon or halogenated hydrocarbon has been found which cannot be emulsified."

Lester Smith gives three rules correlating emulsion type with the *condition* of the soap :—

(1) When the soap is in colloidal solution in the aqueous phase, it tends to stabilise O/W emulsions.

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[1] *J. Soc. Dyers' Colourists*, **48**, 30 (1932).

[2] *J. Phys. Chem.*, **36**, 1401, 1672, 2455 (1932). See also Albert, *J. Soc. Chem. Ind.*, **58**, 196 T. (1939) ; Holmes, *J. Phys. Chem.*, **43**, 495 (1939) ; McBain and Woo, *ibid.*, **42**, 1099 (1938) ; McBain and O'Connor, *J. Am. Chem. Soc.*, **62**, 2855 (1940), and a paper by Bergstermann on a related problem, that of the influence of lipoid solvents in increasing the reaction of formation of addition products between bases and phenol derivatives, *Biochem. Z.*, **304**, 223 (1940). Reference should also be made to the papers by Hartley and by Lawrence in " Wetting and Detergency " (London, 1937) since they expand Lester Smith's theoretical considerations to an important extent.

(2) When the soap is salted out from the aqueous phase, it tends to stabilise W/O emulsions.

(3) When the soap is partially salted out, it may stabilise either type of emulsion, depending on other conditions.

He employs the term " salted out " in the widest possible sense, to cover removal of soap from solution in the aqueous phase, whether by increase in its own concentration, decrease in temperature, or addition of salts of the same or different base. Neither does it matter if the salted-out soap passes into solution in the oil phase, forms a third layer of isotropic solution, or appears as a solid curd insoluble in either phase.

Salted-out soap apparently possesses a feebler power to promote emulsification than soap in aqueous solution, and W/O emulsions are usually coarsely dispersed.

The author concludes with a very clear statement of the position as deduced from his investigations :—

" The most interesting emulsions are the third class, in which the soap is *partially* salted out. By focussing attention on the condition and phase distribution of the soap, rather than on its chemical nature, or on phase volume ratios, the phenomena of inversion receive a simple interpretation. The soap in the two conditions—aqueous solution and salted out—must be regarded as having opposing or antagonistic emulsifying properties ; it is as if there were two emulsifying agents present stabilising, respectively, O/W and W/O emulsions, although in this case they may have the same chemical composition (or they may be soaps of different bases, *e.g.*, Na and Ca). Evidently, when the soap is just beginning to salt out, the emulsion will probably be of the O/W type ; when it is almost completely salted out, it will probably be of the W/O type. Between these two conditions it is not surprising that emulsions of either type can be prepared from the same mixture by different methods of shaking or mixing."

Considerable interest attaches to several other instances of dual emulsions, where the emulsifying agent concerned would theoretically promote only O/W emulsions.

The most striking instance is that given by Seifriz.[1] Using casein as emulsifying agent, Seifriz finds that the type of emulsion furnished by water and hydrocarbon oils depends on the specific gravity of the oil (See Table on p. 245).

The degree of dispersion of the internal phase is finer at the extreme ends of the series, and the emulsions are stable. When the transition from O/W to W/O type occurs, the emulsions are coarse in texture and very unstable.

His explanation, admittedly tentative, was based on the oriented wedge theory and was highly speculative. Other investigators have advanced theories to account for such peculiar results.

Lottermoser and Calantar [2] repeated Seifriz' work using unpurified

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[1] *J. Phys. Chem.*, **29**, 587 (1925). See Keith and Roess, *Ind. Eng. Chem.*, **29**, 460 (1937), and Van der Minne, " Hydrophobic Colloids " (Utrecht, 1937), p. 152.

[2] *Kolloid-Z.*, **48**, 366 (1929).

Commercial Oil.	S.G.	B.P. Range.	Emulsion Type.
Petroleum ether . .	0·699	38—80° C.	O/W
Oleum spirits . .	0·788	144—211° C.	O/W
White kerosene . .	0·822	177—275° C.	O/W
Mineral seal oil . .	0·848	254—350° C.	O/W
Miners' oil . . .	0·874	257—388° C.	O/W—W/O
Straw oil . . .	0·882	283—400° C.	No stable emulsion.
Diamond paraffin . . .	0·886	305—400° C.	W/O—O/W
2900 red oil . . .	0·896	315—400° C.	W/O—O/W
FFF steam-refined cylinder oil . . .	0·918	—	W/O

petroleum containing fractions boiling over the range 75° C.–275° C. Other conditions being equal, the emulsions prepared by a shaking machine were mixtures of W/O and O/W types, whilst those prepared by Briggs' intermittent shaking by hand were all O/W emulsions. The existence of the two kinds of emulsions is now explained as due to the oil containing oil-soluble hydrophobic colloids (particularly in the higher boiling fractions) which tend to promote W/O emulsions, in opposition to the hydrophilic casein.

Wellman and Tartar, referring to Seifriz' experiments, emphasise the increasing viscosity as the density of the fractions increased, with consequent greater difficulty in breaking into drops.

CYBOTACTIC COMPLEXES

Speakman and Chamberlain [1] have discussed the matter from quite a new angle. Certain X-ray investigations have demonstrated that the molecules within liquids continually undergo association into complexes or groups of transitory character. Such cybotactic complexes [2] (or cybomas) remain associated for a brief period, break up and reform other complexes. The idea of Speakman and Chamberlain is that the cybotactic state of the liquids employed is a determining factor in the type of emulsion. In the case of paraffin the tendency to develop structure increases with the length of the hydrocarbon chain. "It seems probable that paraffins of low density give O/W emulsions because little structure is present to resist dispersion; whereas paraffins of high density possess sufficient structure to oppose dispersion, and water becomes the disperse phase." They conclude: "The formation of emulsions, especially in the case of oils and related compounds of high molecular weight, is clearly not determined simply by the magnitude of the interfacial tension and the formation of a stable adsorbed film at the interface. The cybotactic condition of the liquid to be dispersed is of equal importance in ordinary emulsification."

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[1] *Nature*, **130**, 274 (1932); *Trans. Faraday Soc.*, **29**, 359 (1933); *Kolloid-Z.*, **67**, 130 (1934); *Chem. Rev.*, **6**, 483 (1929). See also Drucker, *Physik. Z.*, **29**, 273 (1928); Katzoff, *J. Chem. Physics*, **2**, 841 (1934); Kistler, *J. Phys. Chem.*, **36**, 2948 (1932); Ornstein, *Kolloid-Z.*, **69**, 137 (1934); Krishnan, *Proc. Indian Acad. Sci.*, **1 A**, 211 (1934), and *Phil. Mag.*, **29**, 515 (1940); Parthasarathy, *J. Univ. Bombay*, **5**, (ii.) 16 (1936); Benz, *Proc. Iowa Acad. Sci.*, **41**, 249 (1934).

[2] See Bartell and Mack, *J. Phys. Chem.*, **36**, 65 (1932), who give methods for the independent checking of the theory of cybotaxis.

Hazlehurst and Neville[1] have recently discussed the subject of cybotaxis at interfaces, starting with the conception that the molecular swarms possess a certain shape and rigidity, with a transient existence and surfaces which merge imperceptibly into the completely disorganised liquid environment. An analogy is drawn between a cybotactic group and a crystal in equilibrium with its melt. The intrinsic stability of the groups is a function of the liquid molecules themselves, anisotropic molecules forming the more stable groups.

They argue that while the structure of the surface at a liquid/gas interface is practically only a function of the nature of the liquid, the liquid structure at the boundary between condensed phases (liquid/liquid or liquid/solid) depends upon both phases, and the cybotactic condition will be more pronounced.

Experiments were made on the stability of bubbles and drops at interfaces. Their findings included the observation that bubble stability at a liquid/liquid interface depends upon cybotaxis in the denser liquid. In general, at water/oil boundaries, an air bubble will break through from the water side but not from the oil side ; oil drops will break through from the water side, but usually water drops will not from the oil side.

The authors state that their experimental data show that " if factors other than cybotaxis are eliminated, a W/O emulsion will be more stable than the conjugate system. In the absence of an emulsifying agent there is no reason to conclude from purely energetic considerations that the one or the other system would be more stable, since the interfacial tension is identical in the two systems and the difference in density is likewise a common factor. A difference in stability of the two conjugate emulsions may, however, be predicted if the drops of one liquid penetrate films of the other liquid less readily as a result of cybotaxis in the liquid which constitutes the external phase. By analogy with this reasoning it follows that an emulsifying agent will stabilise that system in which it is preferentially in the external phase."

THE SYSTEM · CRESLYIC ACID/GELATIN/WATER

Woodman has been notable in investigations concerning dual emulsions and has particularly emphasised the influence of the mode of shaking. He[2] observed both types of emulsion in the systems : cresylic acid (or *o*-, *m*- and *p*-cresols)/gelatin/water, marked excess of one liquid phase being the determining factor, this liquid assuming the *rôle* of external phase. Certain instances occurred where both types of emulsion formed when the constituents were not varied in absolute amount, the mode of shaking deciding events.[3] He found that the water-in-cresol type was the more stable emulsion, although the age of the gelatin solution influenced the stability and the type of emulsion.

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[1] *J. Phys. Chem.*, **44**, 592 (1940).

[2] *J. Phys. Chem.*, **30**, 658 (1926). His many papers are summarised in " Technical Aspects of Emulsions " (London, 1935), p. 57.

[3] See *J. Phys. Chem.*, **33**, 88 (1929).

In view of the pecular results obtained, Woodman and Gallagher[1] endeavoured to measure the partition coefficient of gelatin between the two liquids: cresylic acid and water. They point out that in those instances where the constituents of a system, even when maintained in constant ratio, can, by varied means (ageing of one phase or the system, different mechanical treatments, re-shaking) produce both emulsion types, a new partition (temporary or permanent) is to be inferred. Such differences in partition may have very real significance in spite of not being chemically capable of detection, and they arise possibly from *p*H changes, alterations in colloidality of the emulsifier, temporary prevention of the establishment of the true partition due to adsorption, etc.

It was concluded that gelatin is in colloidal solution in both liquids. The partition coefficient, calculated on the simple partition law, is largely in favour of the cresylic acid.

Incidentally, the inclusion of arsenic acid in such systems, intended as sprays for the eradication of prickly-pear, tends to suppress O/W emulsions and to enhance W/O emulsions.[2]

Later work by Woodman[3] confirmed his previous results and explained the dual emulsions as being due to wetting of the colloidal emulsifier by the two liquids. Experimental evidence was secured which seemed to favour the idea of a complex union between cresylic acid and gelatin, " phenols forming some type of complex with the protein by means of the free amino groupings of the latter, and thus providing an alternative emulsifier."

LECITHIN—CHOLESTEROL ANTAGONISM

In view of the great interest taken in the problem of cell permeability, the physiology of fat deposition, and the biochemistry of lipoid materials, much research has centred around lecithin and cholesterol having a bearing on emulsion theory.[4]

Corran and Lewis[5] have investigated the use of the antagonistic emulsifiers: cholesterol and lecithin, at the interface: olive oil/water, studying the influence on the interfacial tension. The lowering effect is additive in the case of mixtures of cholesterol and lecithin, although they promote opposite types of emulsion. With both present in the aqueous phase, inversion of the emulsion occurs when the ratio of cholesterol to lecithin is 1 : 8. If, however, one commences with cholesterol in the oil phase and lecithin in the aqueous phase, the inversion ratio is between 1 : 1 and 2 : 1. Presumably the latter result is the more significant in biological permeability phenomena.

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[1] *J. Phys. Chem.*, **33**, 1097 (1929).

[2] Woodman and Wiley, *J. Soc. Chem. Ind.*, **50**, 187 T. (1931).

[3] *Ibid.*, **52**, 44 T. (1933); **53**, 115 T. (1934).

[4] A comprehensive treatment is given by Degkwitz, " Lipoide und Ionen " (Dresden, 1933), p. 323.

[5] *Biochem. J.*, **18**, 1364 (1924). The problem is also discussed by Leathes, *Lancet* (1925), 803, 853, 957, 1019; Eicholtz, *Biochem. Z.*, **151**, 187 (1924); Pascucci, *Beitr. chem. Physiol. Pathol.*, **6**, 543 (1905); Magat, *Z. ges. exptl. Med.*, **47**, 211 (1925); Rona and Deutsch, *Biochem. Z.*, **171**, 89 (1926); Bernhardt and Strauch, *Z. klin Med.*, **104**, 723 (1926); Liesegang, *Arch. Entwicklungsmech. d. Organismen*, **34**, 452 (1912); Roffo, *Neoplasmes*, **5**, 332 (1926); Epstein and Lorenz, *Z. physiol. Chem.*, **190**, 44 (1930); Cashin and Maravek *Am. J. Physiol.*, **82**, 294 (1927); Jarno, *Arch. Verdauungskrankh.*, **42**, 126 (1928); Califano, *Z. Krebsforschung*, **26**, 183 (1928); Degkwitz, *Ergebnisse Physiol.*, **32**, 822 (1931); Spranger, *Biochem. Z.*, **208**, 164 (1929); Okuney, *ibid.*, **198**, 296 (1928); Dresel and Sternheimer, *Z. klin. Med.*, **107**, 739 (1928); Dahmlos and Solé, *Biochem. Z.*, **227**, 401 (1930); Malquori, *Atti. Congr. naz. Chim.*, **4**, 752 (1933); Labes, *Veröff. Zentralstelle Balneol.*, **1929** (x), 1—19; Remezov, *Biochem. Z.*, **218**, 86 (1930); Eufinger, *Klin. Wochschr.*, **11**, 1144 (1932); Hosaka, *Japan J. Exptl. Med.*, **12**, 455 (1934); Redgrove, *Ind. Chemist*, **13**, 264 (1937).

From Lewis' laboratory, reports have been furnished relating to the physical chemistry of lecithin and cholesterol.[1] Price [2] determined the mobility-*p*H relationship of dispersions of lecithin + cholesterol in equimolecular ratio and found no change in the mobility at various *p*H values or in the position of the iso-electric point of lecithin due to the cholesterol. Hence, the bonds or groups which are responsible for the formation of the lecithin-cholesterol complex cannot be the amphoteric groups of the lecithin or those on which ion adsorption occurs.

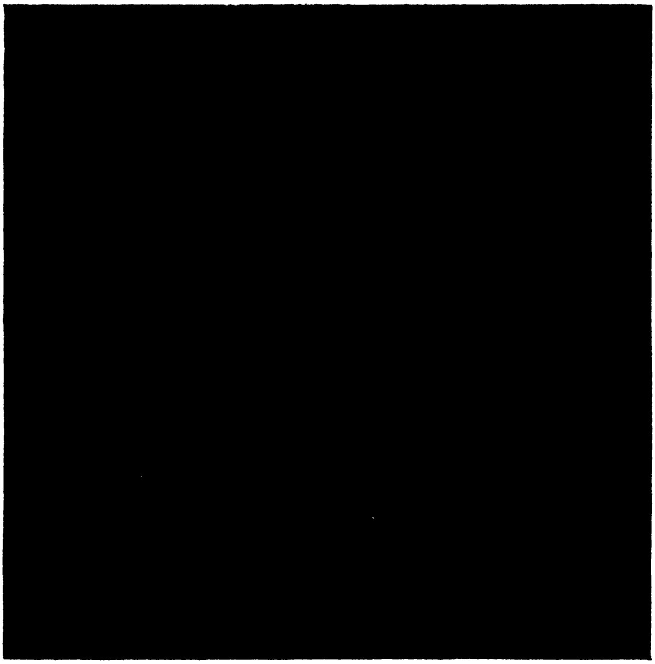

FIG. 43. Photomicrograph of a multiple emulsion (Seifriz).

The function of lecithin as an emulsifying agent has been investigated by Woodman,[3] who found that its hydrosols formed dual emulsions with toluene, benzene, CCl_4, $CHCl_3$, linseed oil, cresylic acid, phenol, hexalin and, possibly, with light petroleum. Oleic acid formed only the W/O type, a surprising result illustrating how the choice of " oil " may alter the expected emulsion type. Bases such as aniline, dimethylaniline, *o*-xylidine and *o*-toluidine furnished only O/W emulsions. The hypothesis was advanced that union of the lecithin with the liquids used and partition of the emulsifier between the liquids might explain the results obtained.

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[1] Price and Lewis, *Biochem. J.*, **23**, 1030 (1929); Jones and Lewis, *ibid.*, **26**, 633 (1932). Cf. Moyer, *Biochem. Z.*, **273**, 122 (1934); Chain and Kemp, *Biochem. J.*, **28**, 2052 (1924); Fishgold and Chain, *ibid.*, **28**, 2044 (1934).

[2] *Biochem. J.*, **27**, 1789 (1933); **29**, 1021 (1935).

[3] *J. Soc. Chem. Ind.*, **51**, 95 T. (1932); **54**, 70 T. (1935).

MECHANISM OF THE PHASE INVERSION PHENOMENON

The most recent and thorough account of the actual mechanism of phase inversion is that given by Schulman and Cockbain (see p. 215) and their argument and accompanying diagrams (Figs. 44 and 45) are reproduced in full.

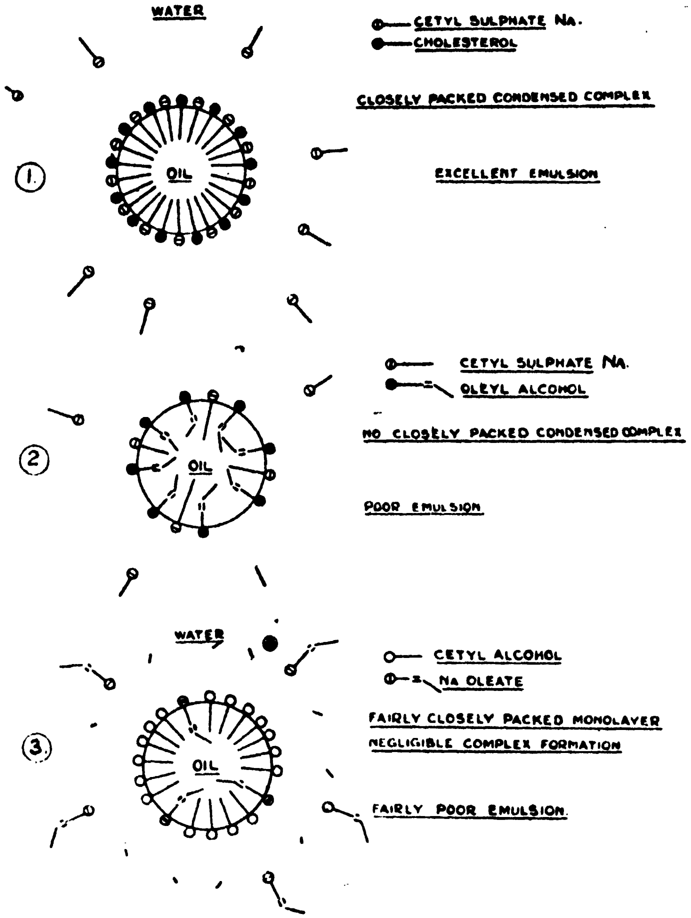
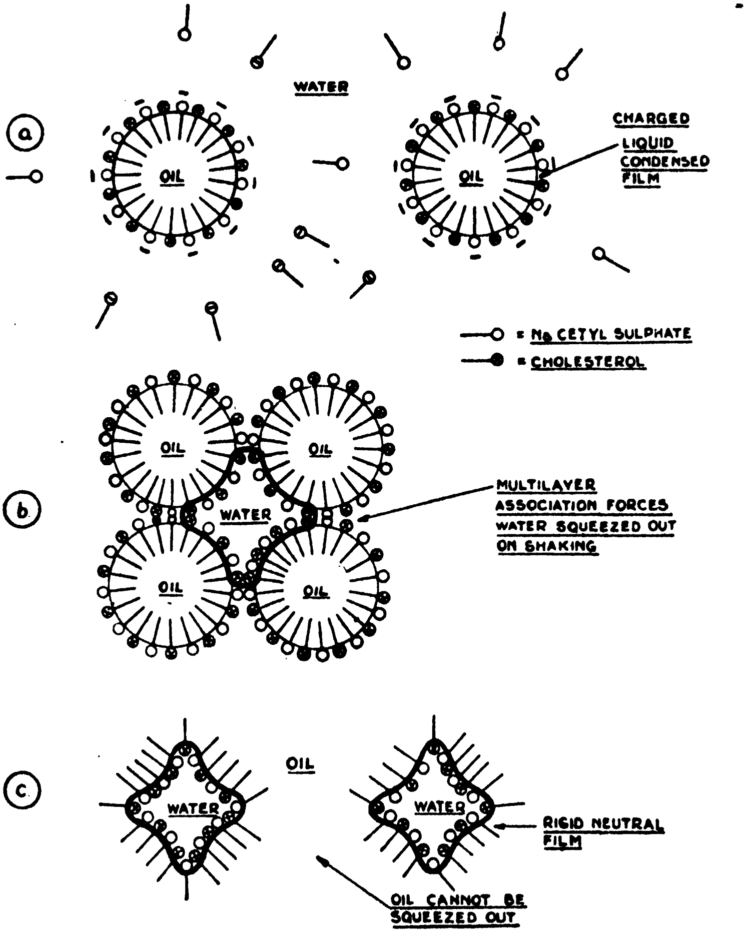


FIG. 44.

"In emulsions of oil in water, the interfacial film is in the liquid condensed state, and is electrically charged. The fact that the water is the continuous phase must mean that the oil droplets are electrically charged; since water, being an ionising medium, enables charged oil droplets to repel one another, owing to the formation of a diffuse layer or ionic atmosphere around the oil droplets, so that a stable oil in water emulsion can be obtained (providing that the physical characteristics of the interfacial film fulfil the conditions already set out). If, however, the oil were the continuous phase, the fact that the interfacial film consisted of charged molecules could not prevent the dispersed water droplets from coalescing because oil being a non-ionising medium, no electrical diffuse layer or ionic atmosphere can be built up. If, furthermore, the charged interfacial film were an interlinked solid, no coalescence would be likely to occur because of mechanical reasons. However, the above film would not be a rigid interlinked solid, since films consisting of charged molecules are either liquid or gaseous, but not interlinked, owing to repulsion between the molecules in the film. Fig. 45*a* shows diagrammatically oil droplets dispersed in water and stabilised by a liquid condensed mixed film such as cholesterol + sodium cetyl sulphate. The adsorbed diffuse double layer of sodium cetyl sulphate is also represented, and the oil droplets are given a negative charge because of the negatively charged cetyl sulphate ions. In Fig. 45*b* is shown the state of affairs after polyvalent cations (Ca^{++} or Ba^{++}, for example) have been added to the oil in water emulsion. Adsorption of the cations has destroyed the


ⓐ
WATER
OIL
OIL
CHARGED LIQUID CONDENSED FILM
—○ = Na CETYL SULPHATE
—● = CHOLESTEROL
ⓑ
OIL
OIL
WATER
OIL
OIL
MULTILAYER ASSOCIATION FORCES WATER SQUEEZED OUT ON SHAKING
ⓒ
OIL
WATER
WATER
RIGID NEUTRAL FILM
OIL CANNOT BE SQUEEZED OUT

I.

FIG. 45.

negative charge on the oil droplets, thus allowing them to coalesce, the diffuse double layer of sodium cetyl sulphate having been removed by cations in the process.

During the process of coalescence, water molecules can be squeezed out from between the oil droplets very readily because the interfacial film molecules have a strong tendency to align themselves with their polar heads together, as in their normal crystal packing.

Fig. 45*b* shows a number of oil droplets in the coalesced state after removal of the charge on the oil droplets. If, now, the interfacial film is rigid, and especially if a cross-linking of the film molecules has occurred to give the crystal packing arrangement described above, the water 'sacks' enclosed by the coalesced oil droplets will themselves be stabilised, and will float away. This process is represented in Fig. 45*c*. The emulsion is now of the water-in-oil type and the interfacial film molecules have their long hydrocarbon chains directed outwards from the water 'sacks.' No coalescence of these water 'sacks' will occur, because the oil cannot be squeezed out from between them. On the contrary, the hydrophobic chains of the film molecules will adhere to the oil molecules of the continuous phase just as ionic head groups in interfacial films adhere to water molecules in emulsions of the oil in water type. Water 'sacks' of irregular shape are typical of all water in oil emulsions, the irregular shape being due to the necessary rigidity of the interfacial film."

DUAL EMULSIONS USING ONE EMULSIFIER

Doubt of the hitherto accepted rule that a given emulsifying agent will only promote one definite type of emulsion has been expressed by Cheesman and King[1] who prepared dual emulsions of amyl alcohol and water with a wide range of agents. In nearly all instances the phase volume ratio and the proportion of emulsifying agent were identical for both types of emulsion.

The authors noted a very curious effect when the mode of mixing was altered, other conditions being constant. Placing all the ingredients in a bottle, vertical jerking rapidly up and down for 10 seconds and then shaking indiscriminately gave O/W emulsions, whilst holding the bottle vertically between the palms of the hands and executing rapid, jerky oscillatory motion about the vertical axis for 10 second followed at once by violent vertical shaking led to W/O emulsions. The pre-wetting of the bottle wall by one liquid seems to promote the type of emulsion where that liquid is the external phase, a phenomenon first described by Ostwald.[2]

To measure stability of the resulting emulsion the authors took the time required for 5 c.c. of the disperse phase to separate when 50 c.c. of the emulsion was placed in a eudiometer of 50 c.c. capacity, the walls of which were wetted with the dispersion medium. The difficulty which the present writer finds with the results of the investigation is the usual one of not being able to assess the influence of the shaking procedure in relation to the industrial methods of effecting dispersion by powerful mechanical means, especially homogenisers. However, as an *indication* that a given emulsifying agent *may* promote dual emulsions, and subject to the proviso that further research is required employing standard mechanical agitation,[1] the authors' collected data are reproduced in Table 36.

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[1] *Trans. Faraday Soc.*, **34**, 594 (1938).

[2] *Kolloid-Z.*, **6**, 103 (1910). See also Andreas, *J. Chem. Education*, **15**, 523 (1938), for results similar to those of Cheesman and King as regards mode of shaking.

TABLE 36

(Abbreviations : *s* = very stable, *i* = very unstable but formation certain, *x* = stability measured with respect to dispersion medium, 0 = no emulsion obtained. Emulsions of the oil in water type are designated O/W, while those of water in oil are W/O.)

Emulsifying Agent.	Stability of O/W Emulsion.	Method of Shaking.	Stability of W/O Emulsion.	Method of Shaking.	Usual Form.
Emulsions of Amyl Alcohol and Water.					
Sodium oleate	*s*	i*a*	5m. 18s. (*x*)	ii	O/W
Oleic acid	2m.	i*a*	4m. 15s.	i*b*	O/W
Magnesium oleate	2m.	i*a*	3m. 55s.	i*b*	W/O
Triethanolamine	10h. (*x*)	i*a*	1m. 36s.	i*b*	O/W
Triethanolamine oleate	*s*	i*a*	1m. 30s.	i*b*	O/W
Saponin	8h.	i*a*	2m. 45s. (*x*)	ii	O/W
Castile soap	*s*	i*a*	18h.	iii*a*	O/W
Rosin soap	2h. (*x*)	i*a*	7h.	iii*a*	O/W
Sulphonated castor oil	*s*	i*a*	6m (*x*)	ii	O/W
Gelatin	*s*	i*a*	40m. 20s. (*x*)	i*b*	O/W
Sodium cetyl sulphonate	5h. 25m.(*x*)	i*a*	5m. 20s. (*x*)	ii	O/W
Finely divided carbon (pigment black)	0*	ii	*i*	i*b*	W/O
Finely divided iron	*i*	i*a*	*i*	iiic	O/W
Finely divided silica	*i*	i*a*	*i*	iiic	O/W
Bentonite (colloidal clay)†	5m. 30s.	i*a*	30s.	ii	O/W
Calcium caseinate	*s*	i*a*	0	ii	O/W
Emulsions of Kerosine and Water.					
Sodium cetyl sulphonate	*s*	i*a*	*i*	iii*a*	O/W
Sodium oleate	*s*	i*a*	2m. 10s.	ii	O/W
Magnesium oleate	20s.	ii	4m. 40s.	i*b*	W/O
Bentonite	—	i*a*	0	ii	O/W
Finely divided carbon	0	ii	*s*	i*b*	W/O

* O/W emulsion prepared with 35 c.c. amyl alcohol, 50 c.c. water and 1 g. charcoal.

† 2 g. bentonite used for the W/O emulsions.

MULTIPLE EMULSIONS

The incidence of multiple emulsions is now well recognised, the dispersed phase itself containing globules of the other phase. Multiple emulsions frequently occur as the result of the inversion of emulsions. Seifriz[2] has demonstrated this matter (Fig. 43), one of his excellent photomicrographs (Fig. 46) showing a quinque-multiple emulsion, where three oil and two water globules alternate one within the other.

There is, however, some recent indication that multiple emulsions can arise from the simultaneous presence in the system of two emulsifying agents of opposite type. Parke[1] prepared such systems, using a mixture of Na and Mg oleates with water and benzene. As he points out, very complicated emulsion systems are to be expected in the presence of dual agents. Woodman[2] also obtained multiple emulsions by the aid of lecithin, which quite possibly contained opposite-type emulsifying agents.

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[1] See, for example, Wilson, *J. Chem. Soc.*, **1934**, 1360 ; King, *Trans. Faraday Soc.*, **37**, 178 (1941).

[2] *J. Phys. Chem.*, **29**, 738 (1925).

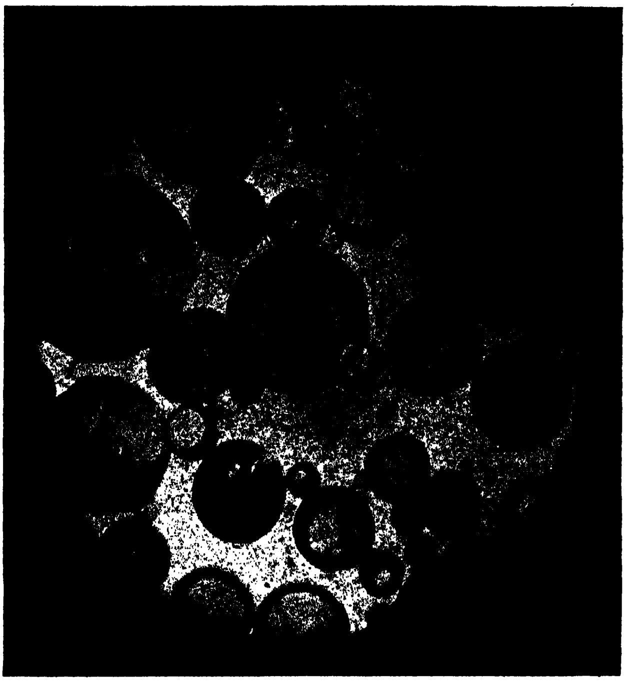

FIG. 46. Photomicrograph of a quinque-multiple emulsion (Seifriz).

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[1] *J. Chem. Soc.*, **1934**, 1112.

[2] *J. Soc. Chem. Ind.*, **54**, 70 T. (1935). See also the paper (in English) by Shemyakin, *Compt. rend. acad. sci., U.S.S.R.*, **14**, 23 (1937).

CHAPTER VIII

EMULSIONS IN BIOLOGICAL INVESTIGATIONS

PHYSIOLOGICAL chemistry is now seriously concerned with the investigation of emulsions, particularly of the blood fat and of the lipoids. In fact, the dispersed fat in the blood, constituting the so-called *chylomicron emulsion*, has been described[1] as the most important emulsion in existence, to which even milk must take second place.

THE CHYLOMICRON EMULSION

In its function of distributing the products of digestion, the blood carries minute globules of fat, termed by Gage[2] *chylomicrons*. A detailed investigation of blood as an emulsion has been reported by Gage and Fish,[3] who fed men and animals with fats and fatty acids mixed with carbohydrates.

Most of the fat of a meal, as soon as it passes through the wall of the intestine, appears in the lacteal vessels as a very finely-dispersed emulsion, the chylomicrons being mainly in the diameter range of 0·5–1μ. The general average size apparently increases, some to 1·5μ, at the height of digestion and absorption. Using a high-power, dark-field microscope, the transport of the fat globules in the lacteals to the thoracic duct and then into the blood stream can be clearly followed. By staining the fatty food material with Sudan III or other oil-soluble dye,[4] which remains in the fatty acids throughout the digestive changes, the final deposition of the fat in the body during the process of assimilation can be observed. The colour is even visible to the unaided eye, the pink colour showing up the fat globules in the lacteals and the blood serum. (Excellent coloured pictures directly from autochrome negatives accompany the authors' paper.)

Many points were investigated and some of the findings were: (*a*) with the dark-field microscope: (1) after eating fatty food, fat globules appear in the blood in ½ to 1½ hours; (2) the time required for the digestion and absorption of fat and then its disappearance from the blood varies from 6 to 10 hours; (*b*) by fat-staining: (1) fat-soluble dyes are only absorbed by the body when attached to a fatty acid radical; (2) after eating fatty food, fat is digested and absorbed and the emulsion appears in the lacteals leaving the intestine of cats and rats in ½ to 1 hour; (3) fat emulsion appears in the thoracic duct in ½ to 1½ hours; (4) chylomicrons appear in the blood stream in 1 to 2 hours; (5) the time after eating fatty food before the pink fat starts to be laid down in the adipose tissue of the body and where it first appears is 2½ hours in rats ; (6) the exact part of the alimentary canal in which absorption occurs and pours the emulsion into the lacteals is mostly near the middle of the small intestine.

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[1] Ludlum, Taft and Nugent, *J. Phys. Chem.*, **35**, 269 (1931); Frazer and Stewart, *J. Physiol.*, **95**, 21 P. (1939); Boyd and Tweddell, *Trans. Roy. Soc. Can.*, 29, Sect. V, 113 (1935).

[2] *The Cornell Veterinarian*, **10**, 154 (1920).

[3] *Am. J. Anatomy*, **34**, 1—77 (1924).

[4] Cf. Myers, MacQuiddy and Baker, *J. Lab. Clin. Med.*, **19**, 462 (1934); Macarthur, *Science*, **72**, 14 (1930).

The subject has also been given attention by Ludlum, Taft and Nugent,[1] who were particularly interested in the nature of the protective film around the globules. Determinations of the isoelectric point of the chylomicrons in human serum were made by a maximum flocculation and a cataphoretic method and the values invariably lay between *p*H 4·6 and 5·4, *i.e.*, between the accepted values from the iso-electric points of serum albumin and serum globulin. There is evidence that the isoelectric point lies between *p*H 4·8 and 5·0. Presumably, therefore, the chylomicrons are surrounded by films of protein, viz., a mixture of serum albumin and serum globulin.

Frazer [2] has recently reviewed the matter and he examined the effect of *p*H change on the fat globules in plasma. " No change is seen in the particles as the *p*H is varied from 7·4 to 6·0. At this point small feathery clumps appear and at *p*H 5·3 complete immobility of the particles occurs. Below *p*H 5·0 normal distribution and mobility of the particles is again evident, and between *p*H 2 and 1 there is a sudden great increase in the number of particles and massive groups of stationary particles accumulate in the field." Frazer concludes that the primary film at the fat/water interface is globulin.

The importance of this observation in physiology is its bearing on the method of assimilation of food fat from the blood and its storage and eventual utilisation. Assuming that the chylomicrons are taken up as such by cells, the physico-chemical character of the surface films assumes primary importance. Thus, acid-fast bacteria with their lipoid-like surfaces are only readily phagocytised when they are treated with the proper serum, which forms a protein film around them. By analogy, the removal of fat from the blood probably depends upon the chylomicrons possessing a surface film of protein which permits wetting by the material of the assimilating cells.

Again, the fat in storage tissues is frequently found as globules much larger than chylomicrons. It is possible that coalescence of the chylomicrons has been brought about by the cell tissues, in which cases there is involved the destruction of the protective protein film, possibly by the action of proteolytic enzymes in the cell.

An interesting example is provided by Kurivagawa [3] and his coworkers under the title " Comparative Studies on the Fat and Lipoid Contents of the Blood in the Right and Left Ventricles." Neither in the fasting nor in the alimentary hyperlipæmic condition is there any difference in comparative composition of blood from both ventricles. In the alimentary hyperlipæmia the plasma from the vena cava superior contains more total lipoid, especially neutral fat, than the blood from the left ventricle. Intravenous injection of fat emulsions results in a higher serum lipoid content of blood from the right ventricle, which is attributed to a mechanical retention of fat globules in the lung.

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[1] *Colloid Symposium Monograph*, **7**, 233 (1930) ; *J. Phys. Chem.*, **35**, 269 (1931).

[2] *Trans. Faraday Soc.*, **37**, 125 (1941). See also Moyer and Moyer, *J. Biol. Chem.*, **132**, 373 (1940).

[3] *Biochem. Z.*, **276**, 336 (1935). See also Locatelli, *Arch. sci. biol.* (*Italy*), **12**, 407 (1928).

FAT ABSORPTION AND METABOLISM

The fate of fats in the body has long provided a favourite subject for research and yet the problem cannot be stated to be completely solved. The first obvious point is that the melting-point of the fat plays an important *rôle.*[1] The upper limit of the melting-point appears to be about 43° C. Hard fats such as beef stearine, M. Pt. 50° C., are absorbed with difficulty, and about 86 to 91 per cent. passes through the alimentary canal unchanged. Butter and oils are digested to about 98 per cent.

Earlier workers stressed the value of providing oils and fats in food in an emulsified state so as to assist ready adsorption. As recently as 1936, Onozaki [2] made histological studies on fat absorption from the large intestine. Using olive oil he noted that the unemulsified oil was not absorbed from the large intestine; whereas the more finely dispersed the oil in an emulsion the greater the absorption. Strangely enough, egg yolk and raw milk were not absorbed, but homogenised milk was absorbed to a pronounced extent. Laboratory studies, such as the relation between substrate dispersion and hydrolysis of fat by enzymes, naturally lend support to this idea.[3]

Important work by Verzar [4] has been used by Smith [5] in his interesting review of fat metabolism in the animal body. Smith's statement is that fat passes through the œsophagus into the stomach and thence to the duodenum and small intestine, where it readily becomes emulsified with the aid of the bile [6] which passes into the duodenum from the liver and gall bladder. Hydrolysis of the emulsified fat follows and glycerol and fatty acids are the result of lipase action. The hydrolytic end products are absorbed by the villi of the small intestine, a portion going directly by way of the portal blood to the liver and the major portion entering the central lacteals, thence to the thoracic duct by which they pass into the general circulation at the junction of the jugular and left subclavian veins.

Channon [7] has drawn attention to the gaps in our knowledge, especially as to why some fat should be made directly available to the liver through the portal circulation when the bulk of the fat passes into the systemic blood. Further, it is not clear what factors determine which fraction of the fat is absorbed into the capillaries and which into the lacteals.

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[1] Von Fejer, *Biochem. Z.*, **53**, 168 (1914); Filinski and Markert, *Compt. rend. soc. biol.* **96**, 344 (1927); Lira and Leyton, *Anales qúim. farm (Chile)*, **1**, 73 (1931); Clayton, "Margarine" (London: 1920), 132.

[2] *Tohoku J. Exptl. Med.*, **29**, 224 (1936); cf. Weiner, *Zeits. Mikroskop. Anat. Forsch.*, **13**, 197 (1928).

[3] Roan and Kleinemann, *Biochem. Z.*, **174**, 18 (1926).

[4] *Nutrition Abstracts Reviews*, **2**, 441 (1933).

[5] *J. Soc. Chem. Ind.*, **58**, 125 (1939).

[6] Verzar and Kuthy, *Biochem. Z.*, **205**, 369 (1929); Furth and Scholl, *ibid.*, **222**, 430 (1930); Coffey, Mann and Bollmann, *Am. J. Digestive Diseases*, **7**, 143 (1940); Crandall and Ivy, *Am. J. Physiol.*, **129**, P. 341 (1940); Hawkins, *Annual Rev. Physiology*, **2**, 259 (1941).

[7] *Annual Rev. Biochemistry*, **9**, 231 (1940).

Frazer[1] has reported experimental data on chylomicron determinations which lead him to a fresh view of the problem.

Whilst Smith summarises the process of the normal digestion and absorption of fats as being in three stages: (1) emulsification and hydrolysis of fat; (2) formation and absorption of the water-soluble fatty acid bile salt complex; (3) liberation of the bile salts and the conversion of the fatty acids to lecithin (much of which is then converted to neutral glycerides), Frazer's view is outlined in the words: "Fat is absorbed both as fat and fatty acid. Absorption of fat favours passage by the lacteal-lymphatic route, by which means it short-circuits the liver and passes more or less directly to the fat depôts. Absorption as fatty acid, on the other hand, is by the capillary pathway, and the material passes direct to the liver *viâ* the portal vein. According to the current hypothesis the fat is broken down, conveyed into the cell, re-synthesised, carried by a detour which avoids the liver, to which it must eventually pass for metabolic use and where it is once more broken down and perhaps re-built into phospholipid. We suggest that a certain proportion passes straight to the liver in a form suitable for building phospholipids or for desaturation, and the remainder, avoiding the liver, passes direct to the fat depôts in a suitably stable form as triglyceride. Further, the fatty acid is absorbed in aqueous solution owing to the hydrotropic action of the paired bile acids, and it is reasonable, therefore, that it should pass by the same route as other water-soluble materials." On this hypothesis, lipolysis cannot be regarded simply as a mechanism for breaking down the fat molecule prior to absorption, but as a factor determining the proportion of the ingested fat passing to the liver for immediate metabolic requirements, thus also determining the quantity diverted to the storehouse for future use.

PARENTERAL ADMINISTRATION OF EMULSIONS

Modern physiological research shows that many workers are concerned with the parenteral administration of fat in emulsion form. Experiments on the injection of emulsions for therapeutic purposes are described by Hedvall,[2] using insulin, and by Strauch,[3] who stabilised olive oil emulsions with metacholestearin and myricin. The intravenous injection of emulsions has been suggested in the treatment of leprosy. Calcagno[4] emulsifies the fat acids of the oils from chaulmoogra and *Carpotroche brasiliensis* with physiological saline, whilst Baranger[5] emulsifies complex esters of hydnocarpic and chaulmoogric acids. The intravenous injection of an emulsion of cod-liver oil and lecithin, or of lecithin emulsion in massive doses, causes a complete disappearance of hepatic glycogen.[6] The possibility of administering vitamin A by the intravenous injection of the emulsified vitamin has been investigated by Groth and Skurnik,[1] who, however, noted that even immediately after injection the blood serum did not show any notable increases in vitamin content. None appeared in the urine and it was concluded that the tissues take up vitamin A with exceptional rapidity. Narat [2] has reported therapeutic benefit in pyelitis and pyelonephritis due to the intravenous injection of an emulsion containing 3·5 per cent. olive oil and 3·5 per cent. lecithin in water. The emulsion presumably acted by production of ketosis, but was tolerated better than the ketogenic diet or ammonium mandelate. Other work is reported on the use of intravenous fat administration to study liver function from the lipæmic curve.[3]

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[1] *Analyst*, **63**, 308 (1938).

[2] *Acta. med. Scand.*, **62**, 334 (1925).

[3] *J. Am. Med. Assocn.*, **92**, 1177 (1929).

[4] *Semana med.* (*Buenos Aires*), **1936**, 798.

[5] *Chem. Abs.*, **34**, 3441 (1940).

[6] Otomo and Nagao, *Tohoku J. Exptl. Med.*, **25**, 63 (1935); Ruffini, *Rass. clin. terap. sci. affini*, **31**, 159 (1932).

Injectable emulsions have of necessity to be very finely dispersed in order to avoid local reactions. Picon [4] has reviewed the subject from this angle, whilst Myers and Blumberg [5] advocate as the most effective method the use of ultrasonic waves (see p. 362).

The early work of Mills [6] concerned subcutaneous injections of emulsions of various edible oils and human fat into cats, using 10 per cent. emulsions. Control tests were made with the oils and fats unemulsified. A group of cats was maintained on a low-protein diet. The absorption of oils or fats was increased from 4—6 times when presented in emulsion form, lard emulsions being especially useful, and about 8 times better absorbed than were the other emulsions. On a high-protein diet, absorption was the same for the clear oils as for their emulsions.

This work was extended by Koehne and Mendel,[7] who employed a cod-liver oil emulsion containing 75 per cent. oil, 23 per cent. water, and 2 per cent. egg lecithin. Subcutaneous, intramuscular and intraperitoneal injections were made into young rats fed on a rickets-producing diet. "Without doubt the rats received considerable protection against rickets from the oil injections. In general, the clear oil was more potent than the emulsion."

The authors raise the question as to a possible connection between the degree of dispersion of an emulsion and its utilisation, but no tests were made on this. The nature of the emulsifying agent would seem to demand special consideration in such therapy, especially for intravenous injections.

Koehne and Mendel aptly summarise the need for investigations along the above lines: "The question whether fat, introduced into the body by ways other than the digestive tract, can be made available for nutritive purposes, has both a scientific and a practical interest. Physiologically it is important to know to what extent the fat molecules so administered must be altered to become suitable for processes of metabolism and to ascertain what capacity the organism possesses for making the requisite changes. Fat has frequently been introduced parenterally, both in animal experiments and clinically, as a seemingly favourable solvent for drugs, or as a vehicle for substances of diagnostic value in X-ray work.[1] Because of its high potential energy content fat has also been injected at times when it has been found necessary to attempt to nourish patients by other than the customary alimentary means." For more extended treatment the student is referred to a highly interesting paper by Bernhardt and Strauch[2] on "Oil-in-Water and Water-in-Oil Emulsions in Their Relation to Medicine."

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[1] *Acta Med. Scand.*, **101**, 333 (1939).

[2] *Urol. Cutaneous Rev.*, **42**, 17 (1938).

[3] Nachlas, Duff, Tidwell and Holt, *J. Clin. Investigation*, **15**, 143 (1936); Virtue and Doster-Virtue, *J. Biol. Chem.*, **133**, 573 (1940).

[4] *J. pharm. chim.* (ix), **1**, 49 (1940).

[5] *Proc. Soc. Exptl. Biol. Med.*, **35**, 79 (1936).

[6] *Arch. exptl. Path. Pharmakol.*, **124**, 334 (1927).

[7] *J. Nutrition*, **1**, 399 (1929).

The question of the selective accumulation of fat which is intravenously injected has occupied several authorities.[3] Using iodipin, Peretti, Reale and Cioglia[4] found that between one-quarter and one-third of the amount of the emulsion given intravenously in dogs is fixed by the lungs, the pulmonary tissue thus attaining a concentration of approximately 1·1 to 0·6 per cent. The value, found immediately after the injection, diminishes within 1½ hours to about 0·3 per cent. and at this concentration persists for some time. This final concentration is independent of the inital concentration and, apparently, represents the capacity of the lung to retain the fat.

Oliaro[5] observed that the fat contents of blood from the left and right heart, peripheral veins and vena cava establish a loss of blood fat in passing through the lungs. The fat content of the lungs increases after a fat meal. It is of interest to note that Francaviglia[6] could find no indication that the lung plays a special part in fat regulation.

Important work has been carried out in Japan on a wide range of issues involved in parenteral administration of fat emulsions. A 20 per cent. emulsion of butterfat, cod-liver oil and lecithin, termed "Yanol," has been used, homogenised and sterilised.

Nomura[7] found that the bulk of the fat in an emulsion intravenously injected rapidly disappears from the blood stream and the remainder disappears at the end of 24 hours. The blood sugar content is unaffected. Using rabbits and injecting 30 c.c. per kg. body weight, there was no observable effect on the blood pressure or the respiration. After a leucopenia of short duration, there ensued a leucocytosis for 5–6 days. Following intravenous injections of oil (10 c.c. per diem for 5 or 10 days), deposition of fat was pronounced in the liver, skeletal muscles and the subcutaneous tissue, but no fat globules were detectable under the microscope and the preformed globules in the parenchyma cells showed no increase in diameter. Dealing with energy change after fat intravenous injection into rabbits (fasting for 1–4 days), there was brought about no change in the respiratory quotient, heat production or the amount of fat oxidised. When, however, the fat stores were depleted by a fast of 7–9 days' duration, the intravenous injection of emulsions caused an increase in the amount of fat oxidised.

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[1] For example, "Campiodol," an iodised rape-seed oil in emulsion form. See Glaser and Kutzmann, *Ann. Surgery*, **90**, 270 (1929); Glaser and Raiziss, *J. Lab. Clin. Med.*, **16**, 943 (1931); *Radiology*, **20**, 471 (1933).

[2] *Z. klin. Med.*, **104**, 723 (1926).

[3] Chierici, *Arch. ital. sci. farmacol.*, **1**, 305 (1932); Scheffer, *Arch. exptl. Path. Pharmakol.*, **124**, 334 (1927); Scheffer and Bodó, *ibid.*, **124**, 326 (1927); Saxl and Donath, *Wien. Arch. inn. Med.*, **13**, 7 (1927); Markowitz and Mann, *Am. J. Physiol.*, **93**, 521 (1930).

[4] *Boll. soc. ital. biol. sper.*, **7**, 984 (1932); *Arch. ital. biol.*, **90**, 59 (1933).

[5] *Z. ges. exptl. Med.*, **91**, 366 (1933). Cf. Kuriyagawa *et al.*, *Biochem. Z.*, **276**, 336 (1935).

[6] *Riv. patol. sper.*, **13**, 45 (1934).

[7] *Tohuko J. Exptl. Med.*, **12**, 247, 389, 497; **13**, 51 (1929). Cf. Baba, *ibid.*, **17**, 154, 274 (1931).

When investigating removal of fat from the blood, after lipæmia (excessive fat in the blood) has been induced by oral administration, the difficulty arises that lipæmia is the resultant of two processes: (1) fat entering the blood, and (2) fat passing from the blood into the tissues. Rony and Mortimer [1] have dealt with this problem, pointing out that the former process is very complicated "depending upon the mobility of the bowel, and upon the rate of digestion and absorption of the fat which in turn depends upon nervous and hormonal factors controlling bile secretion, bile evacuation, pancreatic secretion, etc." Therefore, the authors decided upon intravenous injection of fat, employing emulsions with globules no larger than 4μ and avoiding injections of concentrated fat emulsions at too great a rate, such being physiologically undesirable.

As emulsion, egg yolk was used in physiological saline, so as to contain 1·5 grm. yolk per kg. body weight of the dog under experiment. The fat globules measured from ½–2μ diameter. An advantage gained is that egg yolk emulsion intravenously injected remains in the blood for a prolonged period and permits the investigation of any factors which may possibly influence the removal of the fat.

The emulsion (120 c.c. for smaller dogs and 180 c.c. for larger dogs) was injected at body temperature into the saphenous vein at a constant rate of 2–3 c.c. per minute for 1 hour, using a Woodyatt pump. The fat content of the emulsions varied from 4–5·5 per cent. so as to approximate as near as possible physiological conditions, since following fat meals, at the height of the absorption, fat pours at a similar rate into the blood *viâ* the thoracic duct.

Toleration of the injected emulsions was good. Repeat injections were made within 7 days, thus avoiding protein stock. A sharp rise was observed in the total fatty acid content of the plasma at the end of the injection, followed by a slow disappearance in the succeeding hours. After 5 hours the total fatty acids are yet much above the initial level which is not quite reached even after 20 hours. The rate of removal is quite uniform in all cases. Table 37, reproduced from the authors' paper, illustrates the data.

It is concluded that the rate of removal from the blood of injected fat is much slower than that of fat absorbed from the intestine.[2]

Other routes than intravenously may be employed for the administration of emulsions, and Hotta [3] has studied several and compared the rates of fat removal. When emulsions are given *subcutaneously*, the blood fat rises slowly at first, reaching in 8–24 hours after injection a maximum,

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[1] *Endocrinology*, **15**, 388 (1931).
[2] Cf. Narat, *Am. J. Digestive Diseases Nutrition*, **4**, 104 (1937).
[3] *Tohuko J. Exptl. Med.*, **16**, 311 (1930).

TABLE 37

LIPÆMIA INDUCED BY INTRAVENOUS EGG YOLK ADMINISTRATION

Dog.	Total Fatty Acids, mg. per 100 c.c. Blood Plasma.				
Number.	Before Injection.	At end of Injection.	2 hours after End.	5 hours after End.	20 hours after End.
19	415	659	565	515	—
21	382	775	692	648	—
23	435	831	623	554	457
29	258	702	619	522	—

which is usually twice the original value. It then falls very slowly, still not reaching normal after about 6 hours. With *intramuscular* injection, no significant rise in the blood fat ensues. A barely slight increase is noted in 1–3 hours following the infusion. Similarly, this holds for *intraperitoneal* injection. After 3–5 hours the blood fat is much higher than the original value and in about 24 hours it approximates normal. The absorption of fat is, however, quicker than with subcutaneous injection.

Investigating absorption from serous cavities, Hotta observed very pronounced absorption of fat from infused fat emulsions from the abdominal cavity, the resorption being 64·6 per cent. after 1 hour and 99·1 per cent. after 9 hours. Emulsified fat is rather well resorbed from the pleural cavity, viz. 49·7 per cent. after 1 hour, 81·1 per cent. after 9 hours and 95·3 per cent. after 13 hours.

The resorption of emulsified fats from the large intestine has been studied by Yamakaw, Nomura and Fujinga.[1] From clinical observations of rectal administration it was found that the fat introduced as finely-dispersed emulsion is for the most part, *i.e.*, 80–100 per cent., removed from the large intestine within 24 hours. It was experimentally established that this disappearance is due to absorption through the epithelium of the intestine. Further, it was experimentally shown that the major portion of the resorbed fat goes by way of the lymph tract[2] and only a fraction by way of the blood stream.

Another aspect of the intravenous injection of fat emulsions concerns the immunobiological study of fats. In this connection Tokunoyama [3] has reported on the formation of antibodies against lipoids in tuberculous rabbits.

EMULSIONS AND BACTERIAL TOXINS

Recently great interest has been manifested in the work of Walsh and Frazer [4] on the effects of subcutaneous and intravenous injection of toxins combined with fine emulsions of oils. Toxins, such as diphtheria and tetanus toxins, adsorbed on to oil globules, were found to be non-toxic when injected subcutaneously in large doses.[1] The emulsions used contained 3·5 per cent. of cod-liver, arachis or olive oil in water, using Na_2CO_3 as the emulsifying agent, the finished emulsions being adjusted to *p*H 8. The globule size averaged 0·5–1μ. Similar results have been reported by Myers,[2] who found that olive oil or medicinal paraffin oil emulsions protected against the lethal effects of large doses of the toxins of *B. tetani*, *Cl. welchii* and *Cl. oedamatis maligni* Koch.

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[1] *Ibid.*, **14**, 265 (1929).

[2] Cf. Kimura, *ibid.*, **14**, 275 (1929).

[3] *Ibid.*, **22**, 252 (1933).

[4] *Brit. Med. J.* (March 10, 1934), p. 424; (March 24, 1934), p. 557; *Trans. Faraday Soc.*, **37**, 125 (1941); *J. Pharmacol.*, **67**, (1939); *J. Physiol.*, **87**, 9 P. (1936).

A communication of Walsh and Frazer [3] deals with the use of intravenous injections of olive oil emulsions in the *treatment* of toxæmic conditions, notably pneumonia. The emulson contains 5 per cent. of oil, stabilised with Na oleate (0·2 per cent., brought to *p*H 8 with Na_2CO_3). An adult dose is 15 c.c. Repeated doses are given at six-hour intervals until four injections have been given.

The authors believe that the effect of emulsions in toxæmia is due to adsorption of the toxin on the oil globules, thus preventing it acting upon the body cells. It is likely that the oil globules are removed from the blood stream into the fat depôts, but it is still open to investigation as to the actual fate of the toxin itself.

The present writer is of the opinion that this treatment should be extended to the injection of emulsions which contain oil-soluble bactericides. For instance, hexyl-resorcinol is oil-soluble and a powerful antiseptic. It might prove successful to perform intra-tracheal [4] injection of an emulsion of olive oil containing hexyl-resorcinol, particularly as the tubercle bacilli are regarded as capsulated by a *hydrophobic* material.[5]

FAT-EMBOLISM

Rowlands and Wakeley [6] have lately drawn attention to the incidence of fat-embolism as a complication in war wounds involving simple or compound fractures of the bones and other fat-laden tissues. They discuss the ætiology, post-mortem appearance and the symptoms and physical signs of this phenomenon.

Apparently the capillary bed of the lungs is the first obstructive area to fat after absorption into the circulating blood. According to Groendahl [7] there are two clinical varieties of pulmonary fat-embolism, in one of which the sputum [8] may show fat globules of 10 to 40 μ diameter.

The authors cite suggested methods for emulsifying the blood fat, such as the intravenous injection of a 2 per cent. solution of sodium bicarbonate or a 20 per cent. solution of sodium desoxycholate. The intention is to increase the emulsifying power of the blood and thus diminish the size and obstructive power of the fat globules in the capillaries.[9]

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[1] Cf. Boroff, *Proc. Soc. Exptl. Biol. Med.*, **43**, 294 (1940).

[2] *Brit. Med. J.* (May 26, 1934), p. 945.

[3] " Technical Aspects of Emulsions " (London : 1935), p. 5.

[4] See Cestari, *Boll. soc. ital. biol. sper.*, **9**, 515 (1934), dealing with the electric charge and fixation of colloids injected into the trachea.

[5] Ulzer and Grüber, *Wiss. Mitt. österr. Heilmittelstelle Folge*, **12**, 4 (1934).

[6] *Lancet*, **1941**, 502. See particularly Scuderi, *Surg. Gynec. Obstet.*, **72**, 732 (1941).

[7] *Deutsch. Z. Chir.*, **111**, 56 (1911).

[8] Scott, Kemp and Robb-Smith, *Lancet*, **1942**, 228.

[9] Davis and Goodchild, *J. Chem. Education*, **13**, 478 (1936).

The present writer would suggest that a more rational treatment would be to inject lipase and endeavour to break down the excess fat.[1]

IMPORTANCE OF THE INVERSION POINT

Special importance has been given by several investigators to the incidence of emulsion reversal in biological systems. Thus, Hirschfelder and Serles [2] have dealt with a physico-chemical study of the antagonistic action of Mg and Ca salts and the mode of action of some analgesic drugs.

Their experiments are related to the earlier work of Meltzer and Auer,[3] who showed that the subcutaneous or intravenous injection of $MgSO_4$ into animals caused anæsthesia, which could be immediately relieved by injections of $CaCl_2$. They instance the work of Bancroft, Clowes and Loeb to support the contention that those conditions favouring the promotion of W/O emulsions tend to favour the production of the anæsthetic and analgesic states. Their thesis is that Mg salts tend to increase the water-in-oil type of emulsion more than do Ca salts, due to the much greater solubility of Mg oleate in organic media. "The ordinary soporific drugs and also the 'coal tar' analgesics tend to produce water-in-oil emulsions and thus to diminish ionic interchange between the interior and exterior of the nerve cells."

Peskett,[4] has reported on the effect of salts on cell permeability as shown by studies of milk secretion, his experiments being designed to supply information as to the intimate processes involved in the mammary cells and the mechanism of secretion. Regarded simply, milk is considered to contain two factors, lipoid and non-lipoid, the blood precursors of these two fractions being similarly considered. The supply of these precursors to the cells is a function of the cell permeability to lipoid and non-lipoid materials respectively.

Several factors affect cell permeability, notably inorganic salts such as those of Ca and Na, where antagonistic effects are observed. The process of milk secretion, therefore, offers an opportunity of testing the theory developed by Bancroft, Clowes and Dixon and Bennet-Clark relating to emulsion inversion, since in the present case both lipoids and non-lipoids are simultaneously involved.

Peskett analysed blood samples taken from the jugular vein of cows from 1–3 hours after the morning milking ; corresponding milk analyses were conducted on samples from the bulk evening milk of each cow on the same day as the blood sampling. Determinations were made of Na, total Ca and non-diffusible Ca. The author's results lead him to "a new conception of the cell membrane as a mosaic composed of two types of emulsion, the two phases of which are lipoid and protein. Such a structure would be labile, the pattern of the mosaic being variable under the influence of numerous factors. For example, if the pattern were sufficiently minute it is conceivable that adjacent parts of the membrane might be composed of the two types of emulsion (O/W and W/O) on account of local differences in the proportion of Na and Ca salts, considering the ratio of these in the blood, the low concentration of Ca and the possibility of adsorption effects, etc." Whilst the author's results demand more rigid inquiry, there seems no doubt that a condition of dynamic equilibrium in the cell membrane such as he has postulated is more in harmony with the nature of living processes than a static condition of fixed structure situated at the very entrance to the cell. Mellon [1] has discussed the phase reversal in the bacterial cell wall.

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[1] The *in vitro* hydrolysis of fats by lipase and bile salts is dealt with by Davis, *Proc. Soc. Exptl. Biol. Med.*, **34**, 772 (1936) ; Sym, *Biochem. J.*, **24**, 1265 (1930).

[2] *J. Pharmacol.*, **29**, 441 (1926).

[3] *Proc. Soc. Exptl. Biol. Med.*, 1907–1908, v, 33 ; 1913, xi, 95 ; 1916, xiii, 106.

[4] *Proc. Roy. Soc.*, B., **114**, 167 (1933).

EMULSIFICATION AND ENZYME ACTION

An interesting communication by Wasteneys and Borsook [2] deals with the effect of emulsification in the peptic synthesis of protein. Pepsin added to a concentrated peptic hydrolysate of protein causes the formation of a precipitate of protein. Following a suggestion by Robertson [3] that orientation at cell surfaces could result in reactive groups attaining an effective concentration at the lipoid/water boundary and thus explain the completeness of enzymatic synthesis in living tissues, the authors emulsified the substrate during peptic synthesis. Such emulsifying agents (or rather emulsified materials) as benzene and benzaldehyde proved very effective. Under certain conditions the presence of effective emulsions caused an augmentation of the equilibrium amount of protein synthesised, but under optimum conditions for synthesis no such augmentation of the amount synthesised is effected, although an acceleration of the rate of synthesis is always observed.

A peculiar enzyme phenomenon associated with the emulsion state is exhibited by milk. Shaking raw milk while the fat is in the liquid or partially liquid state activates the lipase naturally present. Hydrolysis of the fat is indicated by the increase in titratable acidity and decrease in *p*H value. Lipolysis induced by shaking will continue after the milk has been cooled to low temperatures. The cause of this accentuated lipolysis is not clear, but Krukovsky and Sharp [4] attribute it to an alteration in the surface characteristics of the fat globules which creates a condition more favourable for lipolysis.

Homogenisation very markedly accelerates lipolysis. Whilst Krukovsky and Sharp state that "activation of lipase by homogenisation and by shaking may be basically the same," it would appear doubtful whether mere shaking can so alter the degree of dispersion of the fat as to compare in any way with the tremendous effect of mechanical homogenisation.[5] Temperature affects the action, maximum fat splitting occurring within the range 41°–51° C.

Schulman [6] has recently presented a most instructive account of the effect of orientation at the oil/water interface of esters and their digestion by pancreatin. Direct analogies were drawn from observations on the adsorption of OH' ions on the ester molecules orientated at the air/water interface to the adsorption of these ions at the oil/water interface. Therefrom was deduced the explanation of the curious specific action of the lipoclastic ferment in pancreatin on its digestion of aliphatic esters which varied in the number of C atoms attached to the alcohol and acid radical hydrocarbon chains.

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[1] *Proc. Soc. Exptl. Biol. Med.*, **23**, 716 (1926).
[2] *Colloid Symposium Monograph*, **6**, 155 (1928).
[3] *Australian J. Exptl. Biol. Med. Sci.*, **3**, 97 (1926).
[4] *J. Dairy Sci.*, **21**, 671 (1938); **23**, 771 (1940).
[5] Gould, *Ind. Eng. Chem.*, **32**, 876 (1940).
[6] *Trans. Faraday Soc.*, **37**, 134 (1941).

Steric factors play a profound influence. It was shown that the length of the alcohol or acid radical chain, especially the latter, plays an important part. "Thus, even with a very short alcohol radical chain (*i.e.*, ethyl) nearly complete inhibition of the digestion of the ester sets in when the acid radical chain consists of 5, 6 carbon atoms or C_6H_5, the digestion of the esters setting in again when the acid radical chain consists of 8 C atoms.

The length of the hydrocarbon chain of the alcohol radical has no influence over the indigestible region, but causes some inhibition over the short and long acid radical hydrocarbon chain region.

Digestible.	*Indigestible.*	*Digestible.*
2—3—4	5—6—C_6H_5	8 Acid Radical.
affected by length of alcohol radical hydrocarbon chain.	unaffected by length of alcohol radical chain.	affected by length of alcohol radical hydrocarbon chain.

Thus butyl and amyl butyrate are more difficult to digest than ethyl butyrate or amyl caprylate than ethyl caprylate. The importance of the nature of the acid radical or alcohol radical chain is well demonstrated by ethylbenzoate or ethyl valerate which are indigestible as compared to benzyl propionate or amyl propionate which are readily digested by pancreatin."

MILK

Cow's milk, a secretion of the mammary gland, is the best known natural emulsion and offers an interesting field for research, not only because of its technical importance, but also because of the variety of questions it raises in colloid physics and chemistry.[1] The present discussion is necessarily confined to those problems which intimately relate to the behaviour of milk considered as an emulsion.[2] Important topics are the nature of the adsorbed film around the fat globules, the viscosity of milk, the size-frequency analyses made by different workers, the phenomenon of cream rising and commercial centrifugal separation, the froth on milk and the whipping of cream, leading to the major problem of the mechanism of butter formation. Long known as such phenomena have been, opinions are still divided on some of the chief points and further research is still called for.

The site of fat synthesis in the mammary gland has been investigated by Kelly and Petersen,[1] who observed that free fatty acid was distributed throughout the epithelial tissue with the greater concentrations in the basal portions of the cells, while the neutral fats were concentrated to the larger extent in the distal portion of the cells. Since there was no evidence that the free fatty acids were present in the form of particles, the authors believe that these acids are present in either molecular or colloidal state. As they are synthesised into neutral fats there is a change in interfacial tension, causing the particles to coalesce so that at the lumen they are of normal milk particle size.

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[1] See Clayton, *Brit. Assocn. Colloid Repts.*, **2**, 96 (1918); Alexander's "Colloid Chemistry," Vol. 4 (New York, 1932), p. 579; Liesegang's "Kolloidchemische Technologie" (Dresden, 1932), p. 862; "Colloid Aspects of Food Chemistry and Technology" (London, 1932), Chap. 7.

[2] Cf. van der Burg, *Lait*, **7**, 452 (1927); Sharp, *J. Dairy Sci.*, **23**, 771 (1940).

THE ADSORBED EMULSION FILM

Milk has the average analysis [2] of 87·27 per cent. water, 3·64 per cent. butterfat, 4·88 per cent. lactose, 3·02 per cent. casein and 0·53 per cent. lactalbumin. That the fat globules should adsorb nitrogenous substances is to be expected from such an analysis. Considerable argument has concerned the question as to whether the fat globules are surrounded by a membrane or by a gelatinous, mucoid, semi-liquid substance, usually referred to under the Danish name (due to Storch [3]) of 'slim-membrane.' Struve [4] considered the membrane to consist of insoluble casein, whilst Babcock [5] believed it to be milk-fibrin. Schmid,[6] Anderson,[7] and Hattori [8] also support the theory of adsorbed protein, the last claiming to have isolated a new protein, 'haptein.'

That the protein content of milk is still not settled is evident from the claims made from time to time concerning the isolation of a 'new' protein therein. Thus, Corran and Green isolated a flavoprotein [9] and Schwartz and Fischer [10] isolated a "hitherto unrecognised protein." Moyer [11] also claims similarly, but recognised that the protein was in complex union with phospholipids. The most thorough study of the milk proteins is by Rowland [12] who reports that the total protein is 3·18 per cent., and the casein : albumin : proteose-peptone : globulin ratios are 23·8 : 2·8 : 1·2 :1·0.

There is now general agreement that associated closely with the milk proteins are phospholipids, the loose chemical ties leading to combinations insoluble in ether but capable of dissociation in alcohol and acetone.[13] The chemical nature of the phospholipid material (isolated from fresh dry buttermilk) has been given by Holm, and his co-workers [1] as lecithin : cephalin : sphingomyelin in the ratio of 8·4 : 4·5 : 1.

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[1] *J. Dairy Sci.*, **22**, 7 (1939). See also Turner, Mo. Agr. Expt. Sta., *Bull.*, 346, 3 (1935).

[2] Cole and Johansson, *J. Dairy Sci.*, **16**, 578 (1933).

[3] *Analyst*, **22**, 197 (1897); *Beretning frä den Kgl. Vet. og Landbohojskole Lab.*, **36**, 1 (1897). *Vide* also the later work of Voltz, *Arch. ges. Physiol.* (*Pflüger's*), **102**, 373 (1904); Abderhalden and Voltz, *Z. physiol. Chem.*, **59**, 13 (1909); Rosengren, *Milch-Ztg.*, **33**, 337 (1904); Rahn, *Forsch. Geb. Milchw. Molkereiwesens*, **1**, 133, 165, 213 (1921); Bleyer and Kallmann, *Biochem. Z.*, **153**, 469 (1924).

[4] *J. Prakt. Chem.*, **27**, 249 (1884); cf. Titus, Sommer and Hart, *J. Biol. Chem.*, **76**, 237 (1928).

[5] *Milch-Ztg.*, **17**, 809 (1888); Richmond, *Analyst*, **22**, 198 (1897).

[6] *Schweiz. Milch-Ztg.*, **50**, 18 (1924).

[7] *Trans. Faraday Soc.*, **19**, 106 (1923); cf. Titus *et al.*, *loc. cit.*

[8] *J. Pharm. Soc. Japan*, No. **516**, 123 (1925); Vol. **49**, 332 (1929); Hattori and Ogimura, *ibid.*, **49**, 147 (1929).

[9] *Biochem. J.*, **32**, 2231 (1938).

[10] *Milchw. Forsch.*, **18**, 53 (1936).

[11] *J. Biol. Chem.*, **133**, 29 (1940).

[12] *J. Dairy Research*, **9**, 30; 47 (1938).

[13] Lobstein and Flatter, *Lait*, **15**, 946 (1935); Tayeau, *ibid.*, **20**, 129 (1940).

Jack and Dahle,[2] dealing with the electrokinetic potential of milk fat in relation to the fat globule membrane, examined the possibility of obtaining information concerning the composition of the membrane by altering the membrane and following the effects of the alterations by electrophoretic measurements. The two general methods to alter the membrane were (1) progressive removal of the membrane from the fat globule surface by centrifugal separation of milk into creams of varying fat content or by washing cream : and (2) by reconstructing a membrane by the adsorption of known milk constituents on the surface of the fat. Casein was the available usable protein employed and synthetic milk, in which a casein layer is adsorbed on the existing phospholipid fat/water boundary, resembled normal milk in the position of the isoelectric point and the slope of the *p*H/mobility curve, suggesting that there is a double layer membrane on the surface of the fat globules.

Palmer and his co-workers have made extended studies of the substances adsorbed on the fat globules in cream, rich in fat.[3] The cream was repeatedly washed with water and reseparated, the solids-not-fat in the cream being thereby reduced to a new minimum on each occasion. The removal of milk solids from the fat is thus secured without breaking the emulsion. " Although the stabilising material that remains concentrated at the fat/water interface may not be the only emulsion stabilising material present in the cream, it is reasonable to suppose that it is the most important."

Palmer and Samuelson [4] found that a phospholipid-like material form the fat globules in washed cream. Churning such cream enabled Wiese and Palmer [5] to show that fresh buttermilk contains a substance capable of stabilising O/W emulsions ; some, at least, of this substance is freed from the surface of the fat globules by the churning process. The material was also recovered from the butter washings and from melted butter. The advantage of subjecting the buttermilk to supercentrifuging instead of extraction by fat solvents is obvious. The supercentrifuged buttermilk was concentrated below 50° C. under reduced pressure to a milky liquid without any precipitation taking place. Dialysis followed against running water for 42—92 hours.

The important result followed that the dialysis results in the fat stabilising material being freed from calcium. Most of the phosphorus [6] in the concentrates remained non-dialysable against water and is in organic combination. The phospholipids were found to be a mixture of mono-amino- and di-amino-compounds. They are associated in the membrane material with a protein which possesses both hydrophilic and hydrophobic characters. This protein which contains N, S and P constitutes the major part of the membrane and is not identifiable with any of the known proteins of milk. It differs from Hattori's "haptein" in having a much lower S content, although the N figure is about the same. The iso-electric point of the membrane material was found to lie at *p*H 3·9—4·0. Detailed analysis of the various milk proteins, including the new membrane protein, have recently been furnished by Wiese and Palmer,[1] who state that preliminary serological studies by Lewis indicate that the new protein possesses specific biological properties.

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[1] *J. Dairy Sci.*, **19**, 632 (1936).

[2] *Ibid.*, **20**, 637 (1937).

[3] For a useful introduction and summary see Rimpila and Palmer, *J. Dairy Sci.*, **18**, 827 (1935).

[4] *Proc. Soc. Exptl. Biol. Med.*, **21**, 537 (1924). Detailed analyses have been furnished by Perlman, *J. Dairy Sci.*, **18**, 113 (1935).

[5] *J. Dairy Sci.*, **15**, 371 (1932) ; **16**, 41 (1933).

[6] Nerking and Haensel, *Biochem. Z.*, **13**, 348 (1908) ; Glikin, *ibid.*, **21**, 348 (1909) ; Dornic and Daire, *Ann. fals.*, **3**, 533 (1910) ; Cusick, Cornell Univ. Agr. Expt. Sta., *Mem.*, **30**, 159 (1920) ; Bischoff, *Z. physiol. Chem.*, **173**, 227 (1928) ; Mai, *Monatsschr. Kinderheilk*, **51**, 391 (1932).

The most recent work by Palmer's school deals with the properties of the membrane material in relation to milk and milk products and goes beyond the scope of emulsions. The original papers [2] should be consulted for accounts of the effect of the adsorption membrane of synthetic creams on the curd tension of milk and on the clotting of milk by rennet.

THE STRUCTURE OF THE MILK SURFACE

Interesting work has concerned the microscopic appearance of milk. Bentivoglio [3] observed a relationship between the protein content of (human) milk and the degree of dispersion of the fat, the higher the protein content the smaller being the globules. He states that the microscopic examination of milk gives an approximate idea of the percentage of protein present.

It is to the work of King,[4] however, that attention is specially directed, since his views are of importance in connection with the problems of butter formation and structure.

King observed the microscopic structure of the surface of milk as revealed with the aid of a vertical illuminator in reflected light at about 540 magnifications. The microscopic picture alters with time. Using milk cooled for some hours prior to observation, it was noted that at 10°–14° C. the surface had individual dark fat globules and clusters, which increased in number as the temperature was raised to 20° C. Clumping was much more marked at 25° C., as the author's photomicrographs beautifully proved. At higher temperatures melted butterfat forms iridescent specks on the surface, the clusters forming lenses.

Centrifuged warm cream showed on its surface round lenses of fat and many small iridescent specks. Cooling the cream to 2°–4° C. for 30 minutes and then warming to 25° C. resulted in practically the same picture as for milk at 25° C.

Skim milk obtained by centrifuging was held at 6°–10° C. for 2 hours. At 10° C. the field of reflected light was almost empty, there being no fat globules or iridescent specks, although scintilating, minute laminæ were seen. In the case of buttermilk from sweet cream the light field at 18° C. swarms with yellow flecks (1–3μ diam.) having saw edges. Interspersed were large iridescent flecks (60–100μ diam.). Noteworthy was the mosaic appearance of the very brilliant interference colours in the midst of some almost non-iridescent, thick fat specks. Clumps with iridescent edges were also seen. After several hours' standing, the larger iridescent flecks aggregated and the interference colours in consequence decreased.

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[1] *J. Dairy Sci.*, **17**, 29 (1934). See also Thurston and Barnhart, *ibid.*, **18**, 131 (1935), and Pedersen, *Biochem. J.*, **30**, 948 ; 961 (1936).

[2] Tarassuk and Palmer, *J. Dairy Sci.*, **22**, 543 (1939) ; **23**, 861 (1940).

[3] *Riv. di Clin. pediat.*, **31**, 3 (1933). The general internal structure of milk is treated by Röder, *Molkerei-Ztg.*, **48**, 342 (1934).

[4] *Milchwirtschaft. Forsch.*, **12**, 500 (1932).

Since the butterfat plays a considerable part in the microscopic structure of the milk surface, it should influence surface tension measurements. Accordingly, spreading experiments were conducted of butter oil on water, skim milk and buttermilk. They showed that between the microscopic fat flecks there is an invisible very thin fat layer of molecular dimensions. King gives the following table, summarising the spreading tests in relation to the microscopic picture of the surface.

TABLE 38

THE SPREADING OF BUTTER OIL ON MILK SURFACES

Liquid Surface.	Surface Picture in the Microscope.	Spreading.
Water . . .	—	Instantaneous spreading.
Skim milk 18°–22° C. .	Free from fat globules and iridescent flecks.	Rapid spreading.
New milk 8°–10° C. .	Some fat globules, no iridescent flecks.	Rapid spreading.
New milk 12° C. .	Moderate number of fat globules and clusters; few iridescent flecks.	Slow spreading.
New milk 14° C. .	Moderate number of fat globules and clusters; iridescent flecks.	Feeble spreading.
New milk 20°–25° C. .	Moderate number of fat globules and clusters—partly melted; many iridescent fat flecks.	No spreading.
Buttermilk < 18° C. .	Numerous iridescent fat flecks and clumps.	No spreading.

Applying the above observations to the phenomenon of churning, King emphasises that well-cooled cream prior to churning shows a surface with only few fat globules and clumps, the picture approximately that of normal milk. The buttermilk therefrom shows a surface full of iridescent flecks, besides incipient clumps. It seems probable that by churning, the butter oil emerges from the fat globules, partly going into the surface, whereby the flecks arise. At the same time, the author's views are confirmed that the butter oil acts as a binding phase in butter.

It is of interest to note that the first wash-water from butter shows a surface like that of buttermilk, decked with very many iridescent specks. (No spreading of butter oil could be observed, cf. buttermilk.) The third wash-water showed still many iridescent flecks, with larger and smaller non-iridescent fat lenses. In contrast with the first wash-water, the third washing permitted slow spreading of butter oil.

In a further study of the surface of milk, King[1] investigated compression phenomena at the surface. If normal milk slowly flows from a pipette into a beaker, the tip of the pipette some height above the surface of the milk in the beaker, so that a fan is formed of a thin layer against the wall, then especially where the fan meets the bulk surface a fine, wrinkled skin develops. Afterwards, the wrinkles disappear, but a visible membrane remains. Even at 25°–30° C. wrinkle formation can be observed, but at 40° C. there appear on the surface only minute pieces of the lamellæ.

A more exact study of the formation of the wrinkled membrane was made by the microscope and reflected light. At 12°–18° C. the surface of the flowed milk showed small, bright flecks in large numbers, and as close neighbours.

THE FAT GLOBULES IN MILK

The fat globules in normal milk range from $0{\cdot}1\mu$ to 10μ in diameter, the average approximating 3μ. The size of the globules varies with several factors, such as breed, lactation period, foodstuff consumed and environmental conditions. The number of the globules is of the order $2\text{–}4 \times 10^{12}$ per c.c.

Numerous workers have reported studies on size-frequency analyses of milks, and an excellent summary of these researches has been given by Campbell.[2] His own work was based on very careful technique (see p. 464), and he found that the fat globules are usually largest during the first two weeks of lactation with the most rapid rate of decline occurring during the next two months. Thereafter, the rate of decline in size is slow but usually continues to the end of the normal lactation period. The mean globule volume at the outset of lactation, during the forty-second week thereof and the averages for the entire lactation in terms of cubic microns were: Guernsey, 28·4, 13·4, 18·8; Holstein, 22·1, 6, 10·4, the former being more variable than the latter. In Guernsey milk approximately 65 to 90 per cent. of the fat globules are less than $3{\cdot}5\mu$ in diameter, with a fairly even division between the 1 and 3μ classes. The portion of the fat globules in Holstein milk under $3{\cdot}5\mu$ in diameter ranges from 70 to 94 per cent. with from 1·5 to 3·5 times as many in the 1μ as in the 3μ class.

Pasteurisation influences the grain-size of the globules in milk, many large globules forming, although the original distribution of the small globules remains almost unchanged.[3]

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[1] *Milchwirtschaft. Forsch.*, **16**, 289 (1934); **18**, 331 (1937).

[2] Vermont Agr. Expt. Sta., *Bull.*, **341**, 1—67 (1932). See also, Rauer, *Arch. Tierernähr. Tierzucht.*, **8**, 246 (1932). Valuable summaries are provided by Rahn and Sharp, " Physik der Milchwirtschaft " (Berlin, 1928), p. 35 *seq.* Photographs of fat globules in various milks are given by Kothavalla, *Indian J. Vet. Sci.*, **7**, 8 (1937); Apple, *J. Am. Vet. Med. Assoc.*, **40**, 331 (1935). Other globule distribution data are reported by Restivo, *Pediatria* (*Riv.*), **43**, 544 (1935), and Sirks, *Dept. Econ. Zaken* (*Netherlands*), *Verslag. Landbouwk. Onderzoek*, **41** C, 28 pp. (1935).

[3] Miss Beckett, *Econ. Proc. Roy. Dublin Soc.*, **2**, 314 (1927). The theoretical considerations of the changes in heated globules of milk fat, from the standpoint of the simple binary system: olein/palmitin, are discussed by Koestler, *Landw. Jahrb. Schweiz.*, **54**, 186 (1940).

SKIM MILK

The milk remaining after cream separation is termed skim milk and contains about 0·15 per cent. of fat, whilst the protein, lactose and ash analysis are similar to those of whole milk.

The size-frequency analysis of the fat globules has been determined by Rahn [1] and his results are given in Table 39 :—

TABLE 39

SIZE-FREQUENCY ANALYSIS OF FAT GLOBULES IN SKIM MILK

Diameter of Globules in μ.	Comparative Number of Globules in Unit Volume.	Percentage of the Total Fat Present in Unit Volume.
0—1	41·8	1·7
1—2	47·7	40·4
2—3	9·2	30·8
3—4	0·9	13·4
4—5	0·3	8·0
5—6	0·1	6·0
6	*Nil.*	*Nil.*

CREAM

Cream is formed by the rising of the fat globules through the denser milk serum to the surface.[2] The density of the liquefied butterfat is about 0·92, whilst that of the milk serum is over unity. According to recent research,[3] the density of the milk of individual cows ranges from 1·027 to 1·039. Thick cream contains about 56 per cent. fat and 39 per cent. water, whilst thin cream contains about 29 per cent. fat and 64 per cent. water. The question of the fat content is of legal importance [4] and for a standard cream the fat content is suggested as 30 per cent., with 45 to 50 per cent. in the case of thick cream.[5]

Using Stokes' law, for a constant medium, the velocity of ascension [6] of the fat globules varies directly as the square of their radius. The Stokes' equation is :—

$$V = \frac{2r^2 (d - d^1)g}{9\eta}.$$

Where V = constant velocity of dispersed phase (globules) in cm./sec.
r = radius of the globules.
d = density of the globule phase (*i.e.*, fat).
d^1 = density of the medium (milk serum).
η = viscosity of the medium.
g = the gravity constant.

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[1] "Physik der Milchwirtschaft" (Berlin, 1928), Chapt. 4.

[2] Sharp, *J. Dairy Sci.*, **23**, 778 (1940).

[3] Hanke, *Milchwirtschaft. Forsch.*, **16**, 220 (1934); cf. Pazzaglia and Zirano, *Ann. chim. applicata*, **24**, 65 (1934).

[4] Stock, *Analyst*, **55**, 535 (1930); Jørgensen, *ibid.*, **56**, 380 (1931).

[5] Elsdon and Stubbs, *Analyst*, **55**, 124 (1930).

[6] Svedberg and Estrup, *Kolloid-Z.*, **9**, 260 (1911).

Van Dam and Sirks,[1] and van der Burg [2] have checked up the rate of ascension of fat globules in milk and found good agreement with values calculated from Stokes' law.

The older view of the creaming of milk will be gathered from the two following quotations from leading authorities: "This separation of fat in the form of cream is possible because of the difference in S.G. between the fat globules and the other constituents of the milk. If the milk is allowed to stand undisturbed, the fat particles will slowly rise to the surface, and can then be skimmed off in the form of cream, the rapidity and completeness with which the fat globules rise to the surface depending on the difference in specific gravity between the fat globules and the other elements in the milk, and on the viscosity of the milk serum." (Stocking.) [3]

"The principal agent retarding or preventing the upward passage of the fat globules is the viscosity of the milk, which is largely due to its . . . constituents of a colloidal nature inherent in milk and cream, and to the milk sugar. If the viscosity of the milk were no greater than that of water, the fat globules would rise to the surface instantaneously in a similar manner as oil poured into water rises to the surface." (Hunziker.) [4]

The work of Rahn has shown the usual view of creaming as given above to be incomplete, and, as regards the viscosity factor alone, quite untenable.

Ordinary gravity creaming may be carried out in three ways :—

(1) Standing the milk in shallow pans to a depth of 2–4 in. for twenty-four—thirty-six hours. The cream is removed by a skimmer, but from 0·5 to 1·0 per cent. of the cream is left in the skim milk.

(2) Standing the milk in deep pans (about 20 in.) set in cold water. The skim milk is withdrawn from the bottom and the amount of fat retained in the skim milk is only about 0·2 per cent. Regarding this method, Bancroft [5] has pertinently remarked: "The dairymen have noticed that, contrary to what one would expect, cream rises more rapidly and more completely in a deep vessel than in a shallow pan.[6] The finer particles of butter fat are caught by the coarser ones and swept upwards because the concentration of the coarser particles per unit of cross-section soon becomes high enough to have a filtering effect." Woodman,[7] working with 50 c.c. of toluene emulsified in 50 c.c. of 0·4 per cent. gelatin solution, found creaming of the emulsions more rapid in wide cylinders. Thus :—

Ratio : $\frac{\text{Internal Diam. of Cylinder.}}{\text{Length of 100 c.c. Column of Emulsion.}}$	Time Required to form a Cream with 66·82 per cent. Oil.
	Mins.
0·7267	27
0·3610	52
0·2410	67

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[1] *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.*, **26**, 106 (1922).

[2] *Forsch. Geb. Milchw. Molkereiwesens*, **1**, 154 (1921).

[3] "Manual of Milk Products" (New York, 1917), p. 225.

[4] "The Butter Industry" (Illinois, 1920), p. 68.

[5] "Applied Colloid Chemistry" (New York, 1921), p. 193.

[6] *Vide* McKay and Larsen, "Principles and Practice of Butter-making" (1906) p. 125.

[7] *J. Pomol. Hort. Sci.*, **4**, 190 (1925).

(3) The water dilution method: To the new milk is added hot or cold water to the amount of ¼ to ⅓ by volume. The idea involved is that lowering the viscosity of the milk serum will expedite the rising of the fat globules. The results, however, are not very good [1] and about 0·7 per cent. of butter fat is lost in the skim milk.

Rahn [2] has shown that the viscosity of milk can be increased, yet instead of the creaming being slowed down it is accelerated. Moreover, the increase in viscosity is attained by adding water-soluble colloids, *e.g.*, gelatin. Using warm milk at 40° C. containing gelatin, Rahn reports: "The addition of gelatin caused a quicker creaming, a thicker cream layer, a looser cream of smaller fat content, a much more complete separation of fat as cream, and also a skim milk of lower fat content, in spite of the fact that the viscosity much exceeded the highest limit for normal milk, which lies about 2·4. These experiments have been repeated with other substances, and even where the viscosity was 5·61, there was a considerably better yield of cream than with untreated milk."

Other colloids, such as gum tragacanth, gum arabic, peptone and albumin in small quantities accelerated creaming. Increasing the viscosity of the milk by adding non-colloids, *e.g.*, sugar,[3] delayed creaming. Obviously these results demand a new interpretation for the phenomenon of creaming.

Rahn further showed that the inhibited creaming of heated milk (formerly explained as due to the loading of the fat globules with coagulated protein) could be changed to a normal value by adding gelatin or other accelerating colloid, after heating. By measuring the velocity of ascent of fat globules in milk, under various conditions, Rahn concluded: "The fat globules in raw milk do not rise singly, but clot together, the clumps possessing buoyancy." In raw milk are numerous such clumps,[4] seldom apparent in heated milk, and herein lies the essential difference in the mode of creaming. Heating was found to destroy clumping of the fat globules; the addition of albumin, gum arabic, and gelatin enhanced clumping due to the formation of an adsorbed glutinous envelope "which makes possible the sticking-together of the globules as they collide owing to their molecular movements." Analytical proof is given of this concentration around the fat globules in the case of gelatin, nitrogen determination being carried out in the cream and skim milk.

Heating reduces the adhesiveness of the envelope-colloid and the fat globules rise singly, a thicker cream layer being the result. In this connection the table shown on the following page given by Rahn,[5] is of interest.

Van Dam and Sirks [6] also found that such colloids as gum tragacanth, gelatin, agar, starch, Irish moss, etc., added to milk, resulted in a 15—25

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[1] Cf. Stocking, *loc. cit.*, p. 228, where the work of Wing on the water-dilution method is discussed.

[2] *Forsch. Geb. Milchwirtschaft*, 1, 133 (1921); *Kolloid-Z.*, 30, 110 (1922).

[3] Leighton and Leviton, *J. Phys. Chem.*, 36, 523 (1932).

[4] See the important earlier work of Henseval, *Rev. gén. lait*, 1, 366 (1902) on fat clustering in milk.

[5] "Physik der Milchwirtschaft" (Berlin, 1928), p. 58.

[6] *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.*, 26, 106 (1922).

TABLE 40

EFFECT OF GELATIN ON THE CREAMING OF RAW AND HEATED MILK

Time Elapsed.	Raw Milk.		Milk heated 10 mins. at 100° C.	
	No Gelatin.	1 per cent. Gelatin.	No. Gelatin.	1 per cent. Gelatin.
0·5 hour . .	3 mm.	8 mm.	*Nil.*	*Nil.*
1·0 ,, . .	9·5 ,,	16 ,,	,,	1 mm.
2·5 hours . .	11 ,,	19 ,,	,,	3·5 ,,
4·0 ,, . .	13 ,,	21 ,,	2 mm.	5 ,,
18·0 ,, . .	16 ,,	28 ,,	3 ,,	16 ,,
48·0 ,, . .	18 ,,	29 ,,	5 ,,	21 ,,
Fat in cream . .	25·8 per cent.	22·5 per cent.	31·1 per cent.	31·2 per cent.
Fat in skim milk .	1·1 ,,	0·3 ,,	2·2 ,,	0·2 ,,
Actual fat in cream .	4·5 grm.	6·50 grm.	1·65 grm.	6·55 grm.
Actual fat in skim milk	2·56 ,,	0·66 ,,	5·39 ,,	0·46 ,,
Degree of creaming .	65 per cent.	91 per cent.	24 per cent.	93 per cent.

per cent. increase in the cream volume on setting the milk at 9° C., although the viscosity increased about 25 per cent. Clumping of the fat globules was postulated. They found no relation between creaming ability and the CaO and H_3PO_4 content of milk. Addition of acid and alkali retarded creaming in the case of fresh milk.

Palmer and Anderson [1] agree that the plasma colloids are more important than the fat globules in relation to the creaming of milks with a uniform fat content. Making a special study of the effect of pasteurisation [2] on creaming, they demonstrated that (*a*) calcium caseinate hinders satisfactory creaming, (*b*) the whey colloids are effective promoters of cream rising, a statement confirmed later by Troy and Sharp,[3] (*c*) pasteurisation increases the hindering action of calcium caseinate. The general conclusion reached is " that both exhaustiveness of rise of fat and greater volume of cream are promoted by the more truly hydrophilic colloids and depressed by colloids with hydrophobic properties. Pasteurisation at 63° C. for 30 minutes increases the effectiveness of the former, but decreases the effectiveness of the latter."

The authors do not agree with Rahn that the explanation of cream rising is to be based on the clumping of fat globules. They emphatically state that this is not the main factor involved. However, no alternative theory is offered, and other workers have since supported Rahn's conclusions with valuable experimental evidence.

Troy and Sharp [4] have published a lengthy paper, accompanied by interesting photomicrographs, strongly supporting the theory that clumping of fat globules underlies creaming. Using known physical constants of milk, a table was prepared showing the rate of rise of *individual* fat globules of various sizes as calculated from Stokes' law. Calculated values show that *contrary to practical experience*, creaming should occur more quickly at 25° C. than at 5° C., *i.e.*, in practice, the globules do not rise singly. Actual experimental determination of the rate of rise of single fat globules agreed well with the rate as calculated from Stokes' law. Thus, the logarithms of the calculated rate of rise when plotted against the logarithms of the diameters of the globules give a straight line graph.

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[1] Minnesota Agr. Expt. Sta., *Ann. Rept.* (1922); *J. Dairy Sci.*, **9**, 1 (1926).

[2] Palmer *et al.*, *ibid.*, **9**, 171 (1926). Cf. Trout and McCan, *J. Agr. Research*, **45**, 483 (1932).

[3] *J. Dairy Sci.*, **9**, 216 (1926).

[4] *Ibid.*, **11**, 189 (1928).

Troy and Sharp next measured the rate of ascent in milk plasma of clumps of fat globules (varying in size from 10 μ to 800 μ), and again the results agreed with those calculated from Stokes' law. The rate of ascent is sufficient to account for the practical experience of creaming. The authors point out that the experimental vision of the clumps is difficult because of their fragile character. Some clumps contain only a few globules, others contain thousands. Agreeing with Rahn and Van Dam and Sirks, Troy and Sharp believe that the clumps contain milk plasma, and the densest spherical clumps probably contain slightly less than 50 per cent. by volume of milk fat. The plasma between is relatively fat free. Deep cream layers contain large irregular stable clumps, whilst " compact approximately spherical clusters, and especially weak clusters, form shallow layers and the fat content of the cream is high." Setting the cream at higher temperatures weakens the clumping effect and permits closer packing. A deeper cream layer therefore results at lower creaming temperatures.

An important technical consideration of the influence of heat on creaming concerns the pasteurisation of milk. An exhaustive study of this subject has been made by Whittaker and his co-workers,[1] who find that pasteurisation : (1) at 61° C. for 30 minutes resulted in a practically unchanged cream volume, or even a slight increase ; (2) at 63° C. for 30 minutes, the cream volume was reduced over a range of about 8 per cent. This was more marked with fresh milk, due to its initial greater cream volume, than with old milk. A good cream volume is favoured by the absence of agitation during the holding period, and by cooling to below 7° C. after pasteurisation. Burri[2] agrees that unheated milk creams more rapidly than milk pasteurised above 61° C. On the other hand, Schneck and Muth[3] found that the separability of milk heated at 61° C. was greater than that of unheated milk, whilst Mertens[4] observed optimum creaming on heating to 60°—61° C.

Rowland[5] in examining the creaming power of heated milk investigated the relationship between the denaturation of albumin and globulin and the reduction in creaming power. Table 41 from his paper is particularly illuminating, the data relating to a duration of 30 minutes heating followed by a creaming period of 4 hours.

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[1] U.S. Dept. Agr., *Bull.*, **1344**,
[2] *Milchw. Zentr.*, **45**, 33 (1916).
[3] *Milchwirtschaft. Forsch.*, **10**, 1 (1930).
[4] *Ibid.*, **14**, 1 (1932).
[5] *J. Dairy Research*, **8**, 195 (1937).

TABLE 41

EFFECT OF HEATING ON THE CREAMING POWER AND ON THE SOLUBILITY OF THE ALBUMIN AND GLOBULIN OF MILK

Temp. of Heating, °C.	Depth of Cream Layer in mm.	Percentage of Total Albumin and Globulin Denatured.
Raw milk	12·3	nil
57·5	14·0	2·7
60·0	15·3	5·5
61·5	13·3	7·4
63·0	10·5	11·0
65·0	5·3	15·6
67·5	2·5	20·5
70·0	2·0	33·4
74·8	2·0	82·0
80·0	2·3	99·1

This worker believes that two factors are concerned in the effect of heat on creaming power, with a temperature of 60° C. as very important. "Clearly, at lower temperatures heating facilitates creaming through the operation of some factor not investigated in the experiment. At higher temperatures a second factor becomes dominant, and with increase of temperature it rapidly reduces the creaming power. This second will be considered to be the denaturation of soluble protein. Some slight denaturation of protein was found at 57·5° C. and more at 60° C., hence the increase of creaming power between these temperatures must be due to the influence of the first factor predominating over the influence of the second."

Rowland's argument then is that creaming is a function of clumping of globules promoted by adsorbed hydrophilic colloids, which in the case of raw milk are quantitatively below the optimum for the promotion of optimum clumping. Accordingly, the addition of such colloids increases creaming in spite of the viscosity increase, whilst removal of the proteins by thermal denaturation reduces clumping and creaming.

The gravity creaming of whole milk has been explained by Sharp and Krukovsky [1] as due to an agglutinin in the milk. The agglutinin is believed to be more strongly adsorbed and to exert its greatest action on the solid or solidifying fat globules. Not being adsorbed on the liquid fat globules it does not clump them. Further, the agglutinin is altered or rendered inactive by heating to 45°—60° C.

Much remains to be worked out concerning the fundamental physico-chemical factors concerned in cream as an emulsion. The peculiar effect of added colloids, as well as the thermal change operating above 61° C., require further investigation. The addition of colostrum, rich in milk proteins, is well known to accelerate creaming of milk. Possibly the earlier investigations of Tiebackx[1] on the mutually flocculating action of two hydrophilic colloids, or the many observations of de Jong[2] on coacervation may provide a clue to the data obtained on accelerated creaming.

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[1] *J. Dairy Sci.*, **22**, 743 (1939); **23**, 771 (1940).

Very exhaustive studies into the creaming of raw and pasteurised milk have been reported by Dahlberg and Marquardt.[3] Pointing out that formerly the gravity separation of cream was employed, the dairy industry was thereby concerned with the complete separation of the fat into the cream layer to reduce to a minimum the fat lost in the buttermilk. Understandable was the fact that Jersey and other milks with large fat globules had the reputation of possessing the best creaming properties. The advent of machine-separated market milk changed the point of view. The problem now became " one of the depth and richness of the cream layer which would form on milk, the distinctness of the cream line or the clarity of the junction of the cream and skim milk, and the influence of heat and handling upon the cream layer ; while the test of the skim milk had become of secondary consideration. Since pasteurisation often reduced the volume of the cream layer, the physical chemistry of cream rising became prominent as a means of obtaining a clue to the restoration of the impaired creaming ability of milk."

The early work of Farrington and Russell[4] showed that pasteurisation at 155° F. (68° C.) caused marked reduction in the cream layer, whereas milk could be held for even an hour at 140° F. (60° C.) and yet retain its capacity for creaming. Detailed tests by Dahlberg and Marquardt led them to state the following essentials for securing the maximum cream layer volumes on pasteurised milk of a given fat content :—

(*a*) The fat globules must be retained in their normal state by avoiding excessive agitation of any kind, freezing, etc.

(*b*) Pasteurisation should be slightly less than 145° F. (63° C.) for a holding period of 30 minutes.

(*c*) Milk should be cooled by a surface tubular cooler to 40° F. or lower, and bottled at once.

(*d*) Sale of the milk should be within 2 to 6 hours, as the cream layer volume shrinks on standing.

(*e*) The milk should be held at 40° F. or lower, since the cream shrinks in volume to a marked degree at 50° F. or higher temperature.

In a further study of the creaming of milk pasteurised at high temperatures, the authors[5] heated a series of lots of mixed herd milk by an internal tubular heater to temperatures ranging from 150° to 165° F. (65° to 74° C.) for periods of time ranging from less than 10 seconds to more than 5 minutes, and the milks set for cream layer determination.

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[1] *Kolloid-Z.*, **8**, 198, 238 (1911); **9**, 61 (1911); **31**, 102 (1922); *Pharm. Weekblad.*, **59**, 574, 1014 (1922).

[2] Summary in *Rec. trav. chim.*, **53**, 163 (1934). See Koets, *J. Phys. Chem.*, **40**, 1191 (1936).

[3] New York State Agr. Expt. Sta., *Tech. Bull.*, **157** (1929), pp. 80. An extensive bibliography is included.

[4] Wisconsin Agr. Expt. Sta., *Report* (1899), p. 129.

[5] *Loc. cit.*, *Tech. Bull.*, **180** (1931), p. 26.

They observed that milk exhibited a heat induction period, there being a period of time wherein the milk could be heated before the temperature began to affect creaming properties. This period, however, varied considerably for different lots of milk.

The authors carefully determined the maximum periods of time that milk can be held at various temperatures with the smallest reductions in cream layer volumes due to heat (amenable to experimental detection), and obtained the following results :—

Temperature (X).	Time held hot in minutes (Y).	
	Observed.	Calculated.
140° F.	90—120	100·2
144	30	30·56
145	15—30	22·76
150	5	5·15
155	1	1·17
157·5	0·75	0·56
160	0·33	0·28
162	0·0	0·15
165	—	0·06

A linear relationship was found between time and temperature when the data were plotted on semi-logarithmic paper with the time plotted on a logarithmic basis. Calculations showed that the maximum period of time that milk can be held at any given temperature to induce the onset of the thermal impairment of the creaming capacity of milk is indicated by the equations :

$$Y = 10^{20{\cdot}0468}e^{-0{\cdot}297X}$$

$$\text{or } \log Y = 20{\cdot}0468 + 0{\cdot}1289X$$

where Y is the time in minutes of exposure to the temperature X° F. Reduction in cream layer volumes due to excessive heat is due to failure of the fat to rise into the cream layer ; the fat content of the cream decreased with increased temperatures or time of heating.

The application of the authors' results to securing the optimum commercial pasteurising of milk has been dealt with in a later communication,[1] which showed that the rate of heating and cooling milk in a pasteurising vat was increased sufficiently to permit vat pasteurisation and cooling of milk with little or no impairment of its creaming properties.

Summarising their extensive data, Dahlberg and Marquardt[2] state that the average cream layer volume forming on fresh raw milk was secured by setting 627 samples of milk from Holstein cows and 900 samples of milk from Jersey cows in an ice-water bath ar 37° F.—40° F. within a few minutes after milking. The cream layer volume, expressed as the percentage which the cream layer volume was of the total volume of milk, was 4·1 times percentage of fat after 24 hours of creaming. The volume was greater after 2 hours and it gradually shrank to a fairly constant value after 24 hours. The mean depth of the cream layers forming on normal milk from Holstein and Jersey cows was directly proportional to the fat content of the milk. Variations in creaming properties were not related to the specific gravity of the milk.

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[1] *Loc. cit.*, *Tech. Bull.*, **189** (1932), pp. 19.

[2] New York State Agr. Expt. Sta., *Tech. Bull.*, **157** (1929), p. 70 ; *Creamery and Milk Plant Monthly*, **20**, (vi), 75 (1931).

A special study was conducted on the creaming capacity of re-made milk, because variation which might be caused by re-mixing skim milk and cream to give a milk for creaming studies does not seem to have had previous investigation. The volume of the cream layer forming on such re-made milk was equal to that of the original fresh milk, providing the milk was fresh and warm at the time of separation, that the skim milk and cream were re-mixed immediately, and that the re-made milk was set at once for cream rising. When the skim milk had been cooled and stored prior to re-mixing with cream, the volume of the cream layer was diminished.

Large variations in the percentage of serum solids in milk had no influence on the cream layer volume. There appeared to be a slight increase in the cream layer volume due to dilution of milk which caused less packing of the cream column and a lower fat content.

Special attention was paid to the incidence of fat clusters in milk and their relation to creaming. " Although the creaming of milk is generally considered to occur by the rising of clusters of the individual fat globules, these clusters are formed through some unknown causative agency which is inherent in the milk plasma." The authors believe that the theory best fitting the complicated facts is a theory of the electric charge on the globules as affected by the calcium ion concentration prevailing.

In newly-drawn warm milk the calcium ions are considered to be at a maximum concentration, and the milk possesses maximum capacity to cream. The clustering is supposed to be due to the effect of the positively-charged Ca ions on the weakly-charged fat globules bearing a negative charge, which normally tends to oppose close union of the globules. Cooling assists clustering because the Brownian movement is reduced. Supporting the theory is the fact that at about 63° C. 71 per cent. of the total CaO of milk is in solution, as against 85 per cent. in the case of the raw milk.[1] This temperature is noted as about the critical for pasteurisation.

It is interesting to note the findings of the authors concerning the fat clusters themselves, as their photographs were particularly good. " The fat clusters in milk of good creaming properties were sufficiently large to be readily visible to the unaided eye when a suitable creaming apparatus was devised for their observation. The clusters varied enormously in size, ranging from a fraction of 1 mm. to several mm. in diameter. The most frequent size was about 0·5 to 1 mm. in diameter. From 8 to 12 minutes were required for clustering to occur and 22—40 minutes for the clusters to rise to give a sharp cream line. The clusters often rose at the rate of 1 in. per minute, but the cream layer became visible when most of the clusters had risen and the time of creaming was governed by the movement of the smaller clusters. The clusters often shrank in volume while rising and retained their identity while packing took place in the cream layer."

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[1] Magee and Harvey, *Biochem. J.*, **20**, 873 (1926); cf. Isaachsen, *Milchwirtschaft. Zentr.*, **61**, 129 (1932). Admittedly there is still much investigation to be done in this connection, as emphasised by Holm, Webb and Dreysher, *J. Dairy Sci.*, **15**, 321 (1932).

CHAPTER IX

MISCELLANEOUS EMULSIONS

BITUMINOUS EMULSIONS

FEW emulsions approach in technical importance the widely-used emulsions of bituminous substances. Their use for road treatment is extensive and increasing, as reflected in the numerous patents granted each year.[1] Essentially the problem is to prepare O/W systems of predetermed degrees of stability in relation to their subsequent contact with road-making materials.[2]

In what follows, fundamental physico-chemical considerations of the emulsions, the numerous emulsifying agents disclosed in the patent literature, and the problem of " breaking " in contact with stones, will be treated. The details of the actual application to road surfaces are beyond the scope of the present volume and have been specially described by others.[3]

DEFINITIONS

The material usually employed in road emulsions is asphaltic bitumen,[4] and the definition now given is that of the British Standard Specification.[5]

Bitumen. Mixtures of natural and pyrogenous hydrocarbons and of their non-metallic derivatives, which may be gaseous, liquid, viscous or solid, but must be completely soluble in carbon disulphide.

Asphaltic Bitumen. Natural or naturally occurring bitumen or bitumen prepared from natural hydrocarbons or from derivatives of natural hydrocarbons by distillation or oxidation or cracking ; solid or viscous, containing a low percentage of volatile products ; possessing characteristic agglomerating properties and substantially soluble in carbon disulphide.

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[1] Summaries of patents are given by : Aladin, " Technisch Verwendbare Emulsionen " (Berlin, 1928) ; Leemans, *Chem. Weekblad.*, **26,** 2 (1929) ; Weiss, *Mineralöle*, **6,** 623 (1933) ; van der Werth, *Asphalt Teer Strassenbautech.*, **34,** 1016, 1037 (1934) and *Kolloid-Z.*, **70,** 124 (1935) ; Calmels, *Papeterie*, **56,** 58 (1934).

[2] See Gabriel in " Technical Aspects of Emulsions " (London, 1935), p. 130 ; Dagnelies, " L'enrobage des pierrailles naturelles au moyen d'emulsion de bitume, bitume fluxe, bitume goudron," (Anvers : De Vos-Van Kleef) ; Weber, *Kolloid-Z.*, **64,** 237, 337 (1933) ; Butterfield, *J. Soc. Chem. Ind.*, **47,** 293 T. (1928) ; Ross, *ibid.*, **48,** 112 T. (1929) ; Garner, *ibid.*, *Chem. Ind.*, **53,** 1000 (1934) ; Kadmer, *Seifensieder-Ztg.*, **62,** 557 (1935) ; Smith, *Refiner Natural Gasoline Mfr.*, **15,** 306 (1936) ; Sirot, *Angew. Chem.*, **49,** 709 (1936) ; Eilers, *Verfkroniek*, **9,** 12 (1936) ; " Bitumen und seine Verwendung im Bauwesen," by Joedicke (Halle, 1937) ; Nishikawa and Hukusima, *Rept. Research Office Pub. Works, Dept. Home Affairs, Japan*, No. **38,** 21 (1937) ; Bardoux, *Congr. chim. ind.*, *Compt. rend.* 18*me congr.*, *Nancy*, **1938,** 43 ; Vellinger and Radulesco, *II*^{e} *Congr. mondial petrole*, 2, Sect. 2, *Phys. chim. raffinage*, **1937,** 659 ; Vellinger, *Bull. assoc. franc. technicians petrole*, No. **46,** 149 (1938) ; Radulesco, *Ann. combustibles liquides*, **13,** 659 (1938) ; *Rev. petrolifere*, **828,** 330 (1939) ; Bennister, *Chem. and Ind.*, **58,** 758 (1939) ; Downing, *Assoc. Asphalt Paving Tech., Proc. Tech. Sessions*, **1939,** 242 ; Gabriel, *J. Inst. Petroleum*, **25,** 531 (1939) ; Foulon, *Allgem. Oel.-u. Fett-Ztg.*, **36,** 167 (1939) ; Temme, *Teer u. Bitumen*, **37,** 3 (1939) ; Stellwaag, *Bitumen*, **6,** 1 (1936) ; Potter and Lee, *Chem. and Ind.*, **57,** 568 (1938).

[3] Wilkinson and Forty, " Bituminous Emulsions for Use in Road Works " (London, 1932) ; Garner, Gabriel and Prentice, " Modern Road Emulsions " (London, 1933) ; Wilhelmi, *Erdöl u. Teer*, **6,** 84 (1930) ; von Skopnik, *Teer u. Bitumen*, **28,** 106 (1930).

[4] Hadert, *Farben-Chem.*, **5,** 12 (1934) ; Fischer, *Teer u. Bitumen*, **28,** 17, 33 (1930) ; Rabate, *Chimie et industrie*, **29,** 766, 1026 (1933) ; a German scheme of classification appears in *Teer u. Bitumen*, **31,** 189 (1933) ; see the comprehensive work by Abraham, " Asphalts and Allied Substances " (New York, 1929), and Spielmann, *Sci. Progress*, **31,** 666 (1937).

[5] No. 434 (1931), p. 5.

Asphalt. Natural or mechanical mixture in which the asphaltic bitumen is associated with inert mineral matter.

Other products are sometimes used in road and other emulsions; thus :—

Lake Asphalt. An asphalt which, as found in nature, is in a condition of flow or fluidity.

Tar. The matter (freed from water) condensed from the volatile products of the destructive distillation of hydrocarbon matter (coal, wood, peat, oil, etc.).

Pitch. The solid or semi-solid residue from the partial evaporation of tar.

Native asphalts probably arose from the action of oxygen or sulphur on mineral oils, mineral and organic matter becoming admixed. The portion soluble in CS_2—asphaltic bitumen—is obtained commercially from mineral (asphalt-base) oils by distillation or oxidation. Admixture of such asphaltic bitumens with earthy materials like sand or stone produces the technically-important artificial asphalts.

COLLOID CHEMISTRY OF ASPHALTS

Asphalt presents a complex colloidal system which has been investigated by Traxler,[1] with special attention to its flow properties,[2] Blokker,[3] Mack,[4] Nellensteyn,[5] and Saal and Labout [6] who deal with the rheological properties. Pfeiffer and Saal [7] believe that the great differences in rheological behaviour accord with the view that asphaltic bitumens consist of dispersons of micelles in heavy, purely viscous oils, the micelles being peptised to different degrees resulting in differences in the tendency to form gels.

From the standpoint of emulsions it is not necessary to recount in detail the fractionation of asphalts into asphaltenes, maltenes, carbenes, and so on, but merely to point out that the physico-chemical behaviour of the dried emulsion films will be profoundly influenced by the character of the asphalt used, since intramicellar elasticity predominates. The usual technical denomination of asphaltic bitumens is one of hardness as measured by the penetration of a standard needle under standard conditions.

INTERFACIAL TENSIONS RELATIONSHIPS

Traxler and Pittman [8] have measured the interfacial tension between asphaltic materials and alkaline solutions, employing the Du Noüy instrument. Determinations were made at 85° C. using two different fluxes: (*a*) derived from a Venezuelan asphaltic petroleum by steam distillation, (*b*) similarly from a Trinidad asphaltic petroleum. Their physical constants were :—

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[1] *Chem. Rev.*, **19**, 119 (1936).

[2] Traxler and Coombs, *J. Phys. Chem.*, **40**, 1133 (1936).

[3] *Angew. Chem.*, **52**, 643 (1939).

[4] *J. Phys. Chem.*, **36**, 2901 (1932).

[5] *J. Inst. Petroleum Tech.*, **14**, 134 (1928); *Kolloid-Z.*, **47**, 155 (1928); *Chem. Weekblad.*, **25**, 190 (1928); Alexander's "Colloid Chemistry," Vol. 3 (New York, 1931), p. 535.

[6] *J. Phys. Chem.*, **44**, 149 (1940).

[7] *Ibid.*, **44**, 139 (1940).

[8] *Ind. Eng. Chem.*, **24**, 1003 (1932).

	(*a*)		(*b*)
S.G. at 85/85° C.	0·9964	..	0·9970
Float at 150° F., seconds . .	44		53
Flash (Cleveland open cup) .	420° F.		415° F.

Against NaOH solutions in water the interfacial tensions were :—

NaOH mol/litre.	Interfacial Tension, dynes/cm.	
	a	*b*
Nil.	16·7	15·7
0·0013	11·4	7·9
0·0025	9·5	5·3
0·0050	5·3	0·0
0·0100	0·5	X
0·0500	X	X

X = spontaneous dispersion at the liquid/liquid boundary.

In accordance with these results, *b* emulsifies more readily than *a* and also gives more stable emulsions. (The importance of alkaline media for dispersion will be noted in the many patents with this as a basic principle.)

Electrolytes in water may complicate emulsification by alkali and, therefore, the influence of NaCl and $CaCl_2$, alone and together, was investigated.

NaCl . . . This was the variable, the NaOH being of constant concentration, 0·005 M for flux *a* and 0·0025 M for flux *b*. The results showed that over a limited concentration range NaCl depresses the interfacial tension, whilst higher concentrations increase it. The minimum is in each case attained when the NaCl is 0·125 M.

$CaCl_2$ . . . This was the variable. As regards NaOH, its constant concentration was 0·01 M for flux *a* and 0·005 M for flux *b*. As the $CaCl_2$ increased in concentration, the interfacial tension also increased, until at 0·0025 M, the interfacial tension became constant. In accord with this, Ca salts cause a decrease in the stability of asphaltic emulsions.

$CaCl_2$ + NaCl . . . The results showed that using NaCl at its concentration most effective in depressing the interfacial tension of flux + NaOH systems, partially overcame the influence of $CaCl_2$ in concentrations less than 0·0025 M. At the point where the $CaCl_2$ and NaCl just balance each other's influence, the ratio $CaCl_2$: NaCl was 1 : 50 (flux *a*) and 1 : 100 (flux *b*). " Although it would appear that NaCl would be of value in overcoming the undesirable effects of Ca salts, again a practical trial showed that the expected advantage did not materialise."

In a further communication, the authors [1] give the results of their measurements of the interfacial tensions between the same two fluxes and solutions of alkaline inorganic salts, namely: Na_2HPO_4, Na_3PO_4, $Na_2B_4O_7$, Na_2CO_3 and Na_2SiO_3. The interfacial tensions were measured at 85° C. and they decreased toward zero as a limit with increasing concentration of the alkaline solutions. In certain instances this decrease is rapid with the interfacial tension becoming very small (Na_3PO_4 and Na_2SiO_3), whereas in other cases the decrease is much less pronounced (Na_2HPO_4 and $Na_2B_4O_7$). Intermediate between these two groups is Na_2CO_3. Flux *b* showed a lower interfacial tension than flux *a* against all of the alkaline solutions.

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[1] *Ind. Eng. Chem.*, **24**, 1391 (1932). See also Mack, *ibid.*, **27**, 1500 (1935).

A reaction at the interface: flux/alkaline solution, was observed in some cases with solutions of higher concentrations. Hydrophilic products were formed which gradually dispersed into the aqueous phase, this becoming opaque. Moderate stirring would then promote emulsification. The concentrations (mol/litre) of Na_2SiO_3 or Na_3PO_4 at which the reaction occurred with fluxes *a* and *b* were 0·0125 and 0·0063 respectively. "The solubility or wettability of the reaction products formed from the alkali present in the emulsifying agent and the acidic constituents of the asphalt has, no doubt, a decided bearing on the type and stability of the emulsion and the ease of emulsification. Experience has shown that flux *b* and asphalts derived from it by steam distillation are more satisfactory for preparing emulsions than flux *a* and its derivatives."

Discussing the effect of the degree of akalinity and the nature of the anion, the authors point out that Na_3PO_4 and Na_2SiO_3 yield solutions much more alkaline than do Na_2HPO_4 or $Na_2B_4O_7$, with Na_2CO_3 intermediate. In many cases, while a pronounced decrease in interfacial tenion occurs, the *p*H value changes only slightly. "If the same flux is used, it seems that the *p*H has less effect on the interfacial tension than does the anion present in the aqueous phase. The phosphate and silicate ions are similar in their effect, and the same is true for the acid phosphate and tetraborate radicals. The effect of the carbonate anion appears to be intermediate between the other two groups."

EMULSIFICATION WITH ALKALI

As will appear, the variety of agents claimed in the patent literature for promoting dispersions of bituminous materials in water is extensive. Prior consideration is given to the use of alkaline media owing to their simplicity and widespread adoption. Again, the use of alkaline media is logical.

An early American specification [1] states: "The object of my invention is to utilise the various resins and resinous substances, such as rosin, the various gums, asphaltum and coal-tar, by rendering them soluble in water, and thus increasing their availability in the various arts and sciences. To effect this, I employ silicate of soda, or soluble glass, which, when diluted to a certain point and heated, is rendered capable of mixing with the melted resin, so as to form a thick paste." It is mentioned that the silicate is diluted to 15° Be. and heated to 100° C. and then the molten material is added with stirring.

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[1] Thomas, U.S. 85,623 (1869).

A notable patent is that of Montgomerie,[1] who adds the molten bituminous material to dilute aqueous NaOH at 100° C. with agitation. He also claims: alkali carbonates or bicarbonates,[2] sodium cresylate,[3] sodium peroxide or percarbonate,[4] phosphates,[5] and the presence of stearine pitch.[6] Further, he claims the addition of sodium laurate to improve wetting and spreading of the emulsion.[7]

Dilute alkali as emulsifying agent is also claimed by Barber [8] and others.[9] Smith [10] mentions trialkali phosphate, a protective colloid and/or borate being added if desired. Hot aqueous silicate solutions are named in several patents.[11] Metallges. A.-G.[12] claim Na_3PO_4 as the emulsifier and after application of the emulsion the addition of $CaCl_2$ to induce breaking. Incidentally, alkali has also been claimed in connection with the dispersion of vulcanised tar [13] and asphalt-tar mixes.[14] Sodium aluminate, zincate or plumbate are also mentioned.[15]

Substances with alkaline reaction are represented by: (1) alkali salts of α- and β- naphthols, pyrogallol or resorcinol or carbazol [16]; (2) alkaline phenoxide [17]; (3) " boron acids in alkaline solution " [18]; (4) casein in the form of alkali caseinate,[19] treated (5) with a solution of acid such as phosphoric or boric to reduce the alkalinity of the caseinate and prevent its deterioration.[20]

Levy [21] claims tannic acid and dilute alkali, whilst crude montan wax in the molten bitumen to assist dispersion in alkali is mentioned in several specifications.[22] (Crude lignite wax is used in preparing stable tar emulsions .[23]) Other patents claim: (1) addition of petroleum heavy oil to the bituminous material before dispersion in alkali[1]; (2) lanolin, bone fat or wool fat, chlorinated or sulphonated if desired, is added to the bitumen prior to emulsification in KOH or K_2CO_3 solution[2]; (3) saccharates of Na, K, Ca, Sr or Ba are employed[3]; (4) the emulsifying agent consists of the alkali salt of a sulphonated oil and possessing an alkalinity within the *p*H range of 11·5—13·2[4]; (5) alkaline materials such as waste iron hydroxide from gas manufacture[5]; (6) fossil diatoms such as kieselguhr with NaOH, preferably in amount less than that equivalent to the SiO_2 in the composition[6]; (7) ground oil-cake is swollen in alkaline water[7]; (8) the crude products obtained by heating humus substances, such as brown coal or peat, with aqueous alkali[8]; (9) alkaline solutions of bleaching powder residues from lubricating oil refining.[9]

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[1] Brit. 226,032 (1923).

[2] Brit. 288,821 (1928). See Poncel, Fr. 832,507 (1938).

[3] Brit. 300,821 (1927).

[4] Brit. 300,415 (1927).

[5] Brit. 300,414 (1927); 427,720 (1935); cf. Halvorsen and Travis, U.S. 1,714,982 (1929) and 1,757,083 (1930).

[6] Brit. 308,051 (1929); Montgomerie and Archibald, Brit. 462,111 (1937); U.S. 2,190,604 (1940). Alkali with rosin pitch is claimed by Tabary, Brit. 445,865 (1936); cf. Thompson and McGivern, Brit. 315,057 (1929); Neitzke, Can. 341,465 (1934); Baume *et al.*, Brit. 255,074 (1925). Waxes are claimed by Kretzer, Ger. 584,695 (1933).

[7] Brit. 305,716 (1927). Turkey-red oil is claimed for a similar purpose in Ger. 527,935 (1929).

[8] Fr. 683,116 (1929).

[9] Krümpelmann, Brit. 25,189 (1906); Lechler, Brit. 392,365 (1933); Jones, Loomis and Banks, U.S. 1,699,536 (1929); Bitumuls Kaltasphalt A.-G., Ger. 499,713 (1925) and 514,485 (1925); Garofalo, U.S. 2,137,975 (1938); Bray and Beckwith, U.S. 2,166,541 (1939); Sweeney and Laughlin, U.S. 2,141,230 (1938); Standard Oil Development Co., Brit. 486,932 (1938); Øvrsgård, Brit. 467,719 (1937); Fr. 810,952 (1937); Minaichev and Bukalov, Russ. 46,651 (1936).

[10] U.S. 1,926,246—7 (1933).

[11] Levy, Brit. 268,411 (1925); Tagg, Ger. 583,237 (1933); Trux, Ger. 505,106 (1927); Smith, U.S. 1,989,775 (1935); Clapp, U.S. 1,787,338 (1930).

[12] Brit. 353,702 (1929).

[13] Main-Gaswerke A.-G. and Hoelzer, Ger. 574,528 (1933).

[14] Ger. 589,960 (1933).

[15] Limburg, U.S. 1,984,023 (1934).

[16] Ness *et al.*, Brit. 350,744 (1930).

[17] Rouault, Brit. 419,358 (1934); Fr. 748,886 (1933).

[18] Chemische Fabrik Buckau, Brit. 298,842 (1928).

[19] Mackay, Brit. 230,177 (1925); Bitumen Investments Inc., Fr. 732,463 (1932).

[20] International Bitumen Emulsions Corp., Brit. 401,131 (1933).

[21] Can. 262,783 (1926).

[22] Neitzke, Can. 323,861 (1932); Kretzer, Ger. 575,104 (1933); Lichtenstern, Austrian 137,894 (1934); Elosequi, Fr. 752,178 (1933).

[23] I. G. Farbenind. A.-G., Fr. 745,113 (1933).

Other alkaline media are: alkaline solutions of hydrophilic colloids,[10] alkali + tannic acid + iron sulphate,[11] phosphatides from soya-beans or fish roes in at least 10 per cent. NaOH,[12] alkali or alkaline-earth salt of an alkyl sulphuric acid, the alkyl radical of which consists of a saturated or unsaturated straight chain of not less than 8 C atoms, *e.g.*, Na cetyl, oleyl, or stearyl sulphate,[13] sulphuric acid derivative of a polymerised fatty acid or a polymerised naphthenic acid,[14] Na salts of petroleum hydrocarbon-aromatic sulphonic acids,[15] by-products from carbonating saccharine juices,[16] the black liquor from the sulphate process of wood-pulp manufacture,[17] gradual *p*H adjustment over the range 7 to 3·5,[18] Na salts of dicarboxylic acids with 2–5 C atoms, *e.g.*, oxalic, malonic or succinic acids,[19] lime,[20] and Turkey red oil.[21]

EMULSIFICATION WITH COLLOIDS

The usual hydrophilic colloids feature in the patent literature; thus: gelatin,[22] glue,[23] resin + glue,[24] casein,[25] casein hardened with

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[1] Société chimique, Ger. 587,829 (1933).

[2] Plauson, Swiss 164,109 (1933).

[3] Bendixen and Morgan, Brit. 346,978 (1930).

[4] Smith, U.S., 1,888,295 (1932); Doutheit, U.S. 1,905,630 (1933).

[5] Rütgerswerke A.-G. and Kahl, Brit. 275,928 (1926).

[6] Bendixen and Morgan, Brit. 330,374 (1929).

[7] Kraft and Heydecke, Ger. 557,228 (1930).

[8] Ges. für Teerverwertung m.b.H., Ger. 591,340 (1934).

[9] Schmitz, Brit. 284,330 (1927) and Ger. 530,420 (1927).

[10] Woodall-Duckham (1920) Ltd. and Arnold, Brit. 506,300 (1939).

[11] Halvorsen, U.S. 1,995,346 (1935).

[12] Schwieger, U.S. 2,020,662 (1935).

[13] E. I. Du Pont de Nemours & Co., Brit. 437,674 (1934).

[14] West and Dodd, Brit. 489,372 (1938).

[15] Thurston, U.S. 2,130,326 (1938).

[16] Ernotte, U.S. 2,047,258 (1936).

[17] Standard Oil Co. of California, U.S. 2,132,607 (1938).

[18] Halvorsen, U.S. 2,157,698 (1939).

[19] Romag A.-G. für Rohmaterialen, Brit. 495,229 (1938).

[20] Robinson and Sutherland, Australian 101,176 (1937).

[21] Firma Paul Lechler, Ger. 648,970 (1937).

[22] Loebel, U.S. 1,960,115 (1934); Colas Products, Ltd., Gabriel and Blott, Brit. 322,792 (1928); Elkington, Brit. 342,296 (1929); S.R.P.I., Brit. 493,898 (1938).

[23] Hailwood, Shepherdson and Stewart, U.S. 1,873,580 (1932); Baume, Chambige and Boutier, Ger. 594,310 (1934); Nakahara, Japan 89,619 (1930).

[24] Disney and Kernot, Brit. 247,142 (1927).

[25] Lutyens and Child, Brit. 238,586 (1924); Kirschbraun, U.S. 1,859,517 (1932).

CH_2O,[1] casein + soaps,[2] starch,[3] starch + tannic acid to *p*H 4—5,[4] starch + soap,[5] alginic acid or alginates,[6] aqueous suspension of cellulose containing alginates,[7] soap + Irish moss,[8] milk, whey, blood, etc.,[9] flax-seed mucilage,[10] bile salts,[11] dyestuffs + complex cyanides,[12] lecithin,[13] cholesterol,[14] cholesterol + boric or phosphoric acid,[15] rubber latex,[16] green acid soap + a farinaceous protein such as corn-gluten meal or soya-bean meal.[17] Other patents deal with : humic acid,[18] gum arabic,[19] heavy metal tannate,[20] viscose.[21]

EMULSIFICATION WITH SOAPS

Various soaps [22] act as efficient emulsifiers for the preparation of bituminous emulsions and the physico-chemical properties of such emulsions have been described by Vellinger and Flavigny,[23] who found maximum stability at *p*H 9—13. Ackermann [24] claims soap and a buffer solution of *p*H about 10.

In addition to the common soaps,[25] various more complex soaps are specified, such as sulphonated oils,[26] sludge sulphonates,[27] rosin soaps + proteins,[28] rosin oil soap,[29] soaps associated with higher monohydric aliphatic alcohols, such as may be derived by reaction of NaOH with sperm oil,[1] or sperm treated with mineral acids.[2] Roualt [3] claims soaps + phenolates + starch meal, whilst soap + casein is the subject of two patents.[4]

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[1] Rodewald, Brit. 393,868 (1932); Geigy A.-G., Ger. 602,165 (1934); Deutsche Vialit-Ges.m.b.H., Ger. 604,328 (1934).

[2] R. Baumheier A.-G., Brit. 379,076 (1932); Lacau, Brit. 400,045 (1933); Parker, Brit. 333,303 (1929).

[3] Levin, U.S. 1,881,729 (1932).

[4] Kirschbraun, U.S. 1,878,974 (1932).

[5] Lister et Cie, Brit. 305,742 (1927); Rouault, Fr. 748,886 (1933).

[6] Gloess and Marini, Fr. 633,687 (1926); Gloess, Fr. 694,905 (1929).

[7] Thornley, Tapping and Reynard, U.S. 1,653,026 (1927).

[8] China and White, Brit. 351,242 (1930); S.R.P.I., Brit. 430,061 (1935).

[9] Erslev, Brit. 225,587 (1924); Kininklijke Stearine Kaarsenfabriek "Gouda," Fr. 581,996 (1924).

[10] Schutte, U.S. 1,950,272 (1934).

[11] American Bitumuls Co., U.S. 1,973,991 (1934).

[12] Braun, Ger. 489,476 (1926).

[13] Hanseatische Mühlenwerke A.-G., Brit. 383,432 (1931) and Ger. 557,154 (1934); 594,189 (1934); Fr. 771,284 (1934).

[14] Mackay, Brit. 233,430 (1924).

[15] Kretzer, Ger. 521,593 (1926).

[16] Colas Products Ltd., Gabriel and Blott, Brit. 329,965 (1929) and U.S. 1,886,334 (1932); Kirschbraun, U.S. 1,988,126 (1935). See "Digest of Patents dealing with Rubber and/or Latex in Road Construction Materials" (London: Rubber Growers' Association 1933), also Martin *et al.*, *J. Rubber Research Inst. Malaya*, **5**, 311 (1934).

[17] Taylor, U.S. 1,932,648 (1933).

[18] I. G. Farbenind. A.-G., Brit. 430,917 (1935); 433,550 (1935); Ger. 627,465 (1936); Klein, U.S. 2,038,572 (1936).

[19] Cox, Brit. 489,373 (1938).

[20] Hixson and Fain, U.S. 2,002,505 (1935).

[21] Levin, U.S. 1,997,868 (1935).

[22] See Berry, Brit. 471,650 (1937).

[23] *Ann. combustibles liquides*, **7**, 217 (1932).

[24] Ger. 584,540 (1933).

[25] Mezger, U.S. 1,762,069 (1930); McSwiney, U.S. 1,384,805 (1921).

[26] Ermen, Brit. 24,135 (1906).

[27] Johansen, U.S. 1,373,661 (1921).

[28] Queck, U.S. 1,867,923 (1932); Michelsen, Danish 38,178 (1927).

[29] Fraser, U.S. 1,259,223 (1918). Rosin is also dealt with by: Sansoube, Fr. 810,310 (1937); Colas Products Ltd., Brit. 441,782 (1936); Fr. 792,874 (1936); Maters and Riemersma, U.S. 2,199,206 (1940); Small, U.S. 2,027,404 (1936); Bert, U.S. 2,136,667 (1938); Padman, Australian 105,993 (1938); Gabriel and Blott, U.S. 2,163,445 (1939).

SOAP FORMATION IN SITU

It is well known that formation of soap *in situ*, having fatty acid in the "oil" phase and alkali in the aqueous phase, confers special advantages in fine dispersion. Dorey [5] has specially emphasised this point. The idea is frequently the basis of patents granted for the preparation of bituminous systems.

According to Mackay,[6] from 2·5 to 5 per cent. of a fatty acid such as oleic acid is added to the molten bitumen, which is then agitated with dilute aqueous NaOH. Silicates or borates may also be used.[7] Stable emulsions are claimed from the use of soft water, pure olein and pure alkali.[8]

Abietic acid with aqueous NaOH is mentioned by Crowne,[9] whilst resin soaps are frequent.[10] Oleic acid with ammonia is claimed by Fair,[11] whilst Steininger [12] claims triethanolamine oleate in a dilute aqueous solution of a water-soluble salt such as K chromate or Na_2CO_3 having a neutral to basic reaction, so that the salt reduces the interfacial tension at the water/asphalt interface.

The molten bitumen may contain sulphonated oil or fat,[13] or it may have linseed oil,[14] the lubricating oil fraction from crude oils,[15] naphthenic acid with or without fatty acid,[16] sebacic acid,[17] or a natural asphalt of high saponification number.[18] The use of an emulsion of a fluid mineral oil is also claimed.[19]

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[1] Fox, Brit. 333,152 (1929).

[2] Fox, Brit. 333,153 (1929).

[3] Ger. 631,781 (1936).

[4] Bray and Beckwith, U.S. 2,022,229 (1935); Salviam Soc. anon., Fr. 817,086 (1937).

[5] "Technical Aspects of Emulsions" (London, 1935), p. 51.

[6] Brit. 202,021 (1923); 202,230 (1923); U.S. 1,542,626 (1925). Cf. Thompson, U.S. 1,884,664 (1932), and 1,861,826 (1932); Lechler, Brit. 333,496 (1929); Tabary, Fr. 775,229 (1934).

[7] Asphalt Cold Mix Ltd., and Gabriel, Brit. 292,251 (1928); Travis and Halvorsen, U.S. 1,757,102—3 (1930).

[8] Asphalt Cold Mix Ltd., Fr. 36,752 (1929).

[9] Australia, 2,185 (1931).

[10] Myers, U.S. 1,957,031 (1934); Main-Gaswerke A.-G., and Hoelzer, Ger. 571,488 (1931); Ges. für Teerverwertung m.b.H. and Kraft, Ger. 549,263 (1929); Wallbaum, Brit. 23,468 (1911); Hay, Brit. 252,260 (1926); Leben and Ormul Products Ltd., Brit. 344,562 (1929).

[11] Can. 345,814 (1934).

[12] U.S. 1,988,879 (1935). Cf. N.V. tot Voorzetting der Zaken Van Pieter Schoen and Zoon, Brit. 381,286 (1932).

[13] Hutton and Fulton, Brit. 252,258 (1926); Elmenhorst, Ger. 295,893 (1916); N. V. Bataafsche Petroleum Maatschappij, Dutch 23,111 (1930); Limburg, Brit. 291,393 (1927); Mackay, Brit. 236,641 (1924); Liberthson, U.S. 1,940,807 (1933); Sparks, U.S. 1,956,779 (1934); Limburg, Ger. 536,912 (1928); Douthett, U.S. 1,905,630 (1933); Gador, Hung. 103,128 (1928).

[14] Van Westrum, Brit. 233,371 (1923); Davey, U.S. 1,294,422 (1919), U.S. 1,472,716 (1924); Mineral Akt.-Ges. Brig., Brit. 276,543 (1926).

[15] La Trinidad, Fr. 636,207 (1926); Limburg, U.S. 1,915,062 (1933); Hepburn, U.S. 1,931,072 (1933).

[16] Mackay, Brit. 233,784 (1924).

[17] Elosequi, Fr. 670,870 (1929).

[18] Bergel, Austrian 134,983 (1933); Ger. 603,801 (1934).

[19] N. V. Mijnbouw-en Cultuur Maatschappij "Boeton," Fr. 726,310 (1931).

Air-blown petroleum asphalt[1] is used as the emulsifier in conjunction with aqueous alkali. (Coal-tar oils are rendered directly emulsifiable with water by slightly oxidising them, as with nitric acid ; such oxidised oils serve to promote dispersions of bitumen in water.)[2] Cross and Engelstad[3] claim the use of a non-gelatinised concentrated solution obtained by the action of chromic acid on a concentrated solution of the soluble lignone derivatives obtainable by the treatment of wood substance with H_2SO_3.

According to Smith[4] an O/W bitumen emulsion is produced by the addition of a salt of a metal of the third analytical group, such as Fe, Al or Cr sulphate to an approximately equal quantity of concentrated waste sulphite liquor, followed by use of the resulting product as an emulsifying agent. Turpentine oil[5] has been named as the sole emulsifying agent for bitumen dispersions, as also the pitchy product from the evaporation of sulphite liquor.[6]

EMULSIFICATION BY SOLID POWDERS

A number of patent specifications deal with the use of solid powders as emulsifying agents for the preparation of bituminous emulsions. Thus : dry brown coal,[7] oil shale[8] ; coal + 0·1 per cent. of a salt which forms a highly insoluble Ca salt even in the presence of CO_2, *e.g.*, the fluoride, oxalate or fluosilicate of Na or K[9]; plastic mud from rivers (for tar emulsions)[10] ; lime wash or other calcareous substances[11] ; Portland cement with or without colloidal $Al(OH)_3$[12] ; gelatinous metallic oxides + asbestos[13] ; silica or slate dust with tannic acid or soap[14] ; slate dust, silica, barytes, marble dust, powdered calcite, fibrous talc, ZnO, precipitated $BaSO_4$ or the like with substances such as basic sulphates of Cu or Fe[15] ; ground mineral phosphate[16] ; fine silica with an insoluble hydroxide in finely-divided form such as $Al(OH)_3$ and a peptizer for the hydroxide such as $AlCl_3$[17] ; a protein + finely-divided colloidal $Al(OH)_3$[18] ; sulphite cellulose lye and colloidal silica[19] ; tannic acid is mixed with finely-divided solid material such as asbestine or gilsonite, which is readily wetted by the bituminous material to yield a plastic mass with water, this serving as the emulsifying agent for bitumen.[1]

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[1] Malchow A.-G., Ger. 542,148 (1927) ; Naamlooze Vennootschap Bataafsche Petroleum Maatschappij, Dutch 14,751 (1926).

[2] Verkaufsvereinigung für Teererzeugnisse G.m.b.H., Ger. 518,394 (1926) ; Chemische Fabrik Flörsheim H. Noerdlinger A.-G., Ger. 566,670 (1929).

[3] U.S. 1,878,828 (1932).

[4] U.S. 1,895,775 (1933).

[5] Mayer and Uddeholms Aktiebolaget, Brit. 365,844 (1931).

[6] Deutsche Vialit G.m.b.H., Ger. 590,723 (1934).

[7] I. G. Farbenind. A.-G., Brit. 362,467 (1930) ; Roederer, Fr. 727,328 (1931) ; Brit. 395,384 (1933).

[8] Roederer, Brit. 402,891 (1933) ; Ger. 608,431 (1935).

[9] Lefebvre and Berger, Brit. 362,299 (1931).

[10] Kolloidchemie Studienges, Carpzow and March, Brit. 372,917 (1932).

[11] Tagg, Brit. 388,093 (1933).

[12] Kirschbraun, U.S. 1,959,586 (1934) ; Lewis, U.S. 1,783,365 (1930).

[13] Lewis, U.S. 1,787,418 (1930).

[14] Lewis, U.S. 1,869,379 (1932).

[15] Lewis, U.S. 1,869,380 (1932).

[16] Lewis, U.S. 1,869,382 (1932).

[17] Lewis, U.S. 1,869,381 (1932).

[18] Moser, U.S. 1,759,913 (1930).

[19] Geigy A.-G., Brit. 307,000 (1927).

Ebberts[2] points out that silica, Fe oxide and gypsum promote O/W systems with bitumen, but limestone, $MgCO_3$, $Ca(OH)_2$ and $Mg(OH)_2$, and Portland cement promote W/O emulsions.

EMULSIFICATION BY COLLOIDAL CLAY

The remarkable power of colloidal clay to promote O/W emulsions finds extensive reference in the patent literature dealing with bituminous emulsions.[3]

According to Miller[4] a natural solid bituminous base which is self-emulsifying by reason of the presence of an associated impurity, such as that of a clayey nature in Trinidad Lake asphalt, is finely ground in its native state with water to yield an O/W dispersion. Bentonite is featured in several specifications,[5] its thorough peptisation by colloid mill treatment being advocated.[6] Finely-ground kieselguhr is recommended for tar-bitumen mixtures for road use.[7]

Peptisation of the clay by various means includes: the use of tannin[8]; the addition of soap or saponin[9]; addition of naphthenic soap[10]; employing agents which will saponify *in situ*;[11] addition of humic acid[12]; admixture with MgO or $Mg(OH)_2$[13] or a more simple alkali.[14] Kirschbraun[15] renders the emulsions more mobile by the addition of a small quantity of a substance having not less than one OH group and/or COOH group, *e.g.*, citric acid. Adjustment of the *p*H to an optimum value for peptisation of the colloidal clay and for optimum emulsification is also claimed.[16]

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[1] Kirschbraun, U.S. 1,832,987 (1931).

[2] *Rock Products*, **33**, (xxiv), 53 (1930).

[3] Cf. Bray and Beckwith, U.S. 2,137,226 (1938); Fain, U.S. 2,027,582 (1936); Lechler, Brit. 443,666 (1936); Akt. f. Komisk Industri, Dan. 50,735 (1935); Smith, U.S. 2,099,351 (1937); Reiner, Ger. 611,491 (1935); Chandeysson, Fr. 775,906 (1935); Lister, Brit. 436,494 (1935); Smith, U.S. 2,033,657 (1936). Spent fuller's earth is mentioned in Thurston, U.S. 2,037,669 (1936) and Kauffman, *Natl. Petroleum News*, **27**, No. 52, 25 (1935); **28**, No. 1, 21 (1936). Clay + lime is claimed in Frunzetti, Brit. 494,380 (1938); Groskopf, U.S. 2,104,077 (1938).

[4] U.S. 1,752,449 (1930). Cf. Porkess, U.S. 1,240,253 (1917).

[5] Reeve, U.S. 1,398,201 (1922); F. Raschig G.m.b.H., Ger. 495,232 (1927); N. V. Bataafsche Petroleum Maatschappij, Brit. 341,443 (1929); Kirschbraun, U.S. 1,417,835 (1922), 1,479,042 (1924), 1,620,899—90 (1927), 1,679,475 (1928), 1,707,809 (1929), 1,734,437 (1929), 1,829,722 (1931), 1,948,881 (1934), 1,969,308 (1934), Brit. 244,135 (1925), 286,844 (1927); Hurrell, Brit. 315,495 (1928); Gundlach, U.S. 1,663,652 (1928); Jones, Loomis and Banks, U.S. 1,699,537 (1929); Hall and Mortell, U.S. 1,882,834 (1932); Illemann, Brit. 105,202 (1917). Colloidal clay is used for tar and pitch emulsions: Austrian 116,390 (1929).

[6] Fain, U.S. 1,963,231 (1934); see also Russian 31,751 (1933).

[7] Francois, Fr. 751,956 (1933).

[8] Kirschbraun, U.S. 1,869,697 (1932).

[9] N. V. De Bataafsche Petroleum Maatschappij, Brit. 342,031 (1929), and Fr. 684,531 (1929); Fain, U.S. 1,793,918 (1931).

[10] Cushman, U.S. 1,913,430 (1933); Billinghame, Brit. 252,449 (1926).

[11] Ges. für Teerstrassenbau. m.b.H., Ger. 542,605 (1926); Brit. 387,825 (1933); Bitumen Investments Inc., Fr. 744,008 (1933).

[12] I. G. Farbenind. A.-G., Brit. 381,933 (1932); Schilling, Ger. 593,121 (1934).

[13] Montgomerie, Brit. 321,334 (1928); Lewis, U.S. 1,783,366 (1930).

[14] Hutzenlaub, U.S. 1,957,408 (1934); Firma Paul Lechler, Ger. 601,891 (1934), Ger. 553,245 (1929), Brit. 392,365 (1933); Thompson and McGivern, Brit. 315,057 (1928).

[15] U.S. 1,918,759 (1933).

[16] The Flintkote Co., Ger. 582,794 (1933); Brit. 321,721 (1929); N. V. De Bataafsche

MISCELLANEOUS EMULSIONS

A number of patents of special interest deal with varied aspects such as slow-breaking emulsions to act as binders,[1] quick-breaking emulsions,[2] incorporation of rubber latex,[3] emulsions of high viscosity attained by the presence of polyhydric alcohols such as glycol and glycerol,[4] mixed O/W emulsions,[5] and W/O systems.[6] Whilst the still residue from the purification and fractionation of light oil derived from the by-product coking of coal will serve as an emulsifying agent for W/O emulsions,[7] it is possible to invert an O/W type by the addition of aluminium sulphate.[8]

Traxler [9] has described the consistency of concentrated emulsions of bitumen and his paper is of interest in connection with the patent by Terrey, Gabriel and Blott [10] who claim emulsions of desired viscosity by the technique of mixing systems of different size-frequency analysis. Related to this is the idea of Kirschbraun [11] who mixes stable and unstable emulsions with adjustment of the *p*H value.

THE ADHESIVITY PROBLEM

The major use of bituminous emulsions is to bind materials, particularly to prepare road surfaces.[12] Considerable discussion has centered round this apparently simple matter, mainly in connection with the possibility of pre-estimating the factors operating to yield a binding film of bitumen between and on stone material.[13]

That the emulsion must " break " in contact with stone is a prerequisite to film formation, but even now investigators are concerned with devising suitable laboratory tests, which at first were primarily

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Petroleum Maatschappij, Brit. 312,580 (1930) and Fr. 683,991 (1929); cf. Brit. 341,914 (1928) and Brit. 334,100 (1929); Painter, U.S. 1,793,957 (1931); patents by Kirschbraun are: U.S. 1,691,766 (1928); 1,691,767 (1928); 1,691,768 (1928); 1,733,494 (1929); 1,733,495 (1929); 1,733,496 (1929); 1,960,112 (1934).

[1] Boneysteele and McKercher, U.S. 2,135,866 (1938); Bray and Beckwith, U.S. 2,080,689 (1937).

[2] Watts, U.S. 2,040,115 (1936); Hewes and Chappell, U.S. 2,083,498/9 (1937).

[3] Svensson, U.S. 2,037,948 (1936); Mannheimer, Brit. 464,562 (1937); Davis, Brit. 489,847/8 (1938).

[4] Colas Kaltasphalt G.m.b.H., Ger. 674,899 (1939).

[5] Daimler, U.S. 2,041,234 (1936).

[6] Rouault, Brit. 421,269 (1934).

[7] Carmody, U.S. 2,195,529 (1940).

[8] Sadtler and Field, U.S. 2,013,972 (1935). See also Bray, U.S. 2,041,279 (1936); T.I.C. Research Co. Ltd., Brit. 465,589 (1937).

[9] *Ind. Eng. Chem.*, **28,** 1011 (1936).

[10] U.S. 2,009,821 (1935).

[11] U.S. 2,061,076 (1936).

[12] Latzko, *Petroleum Z.*, **31,** (xi), 4 (1935); Ingersleben, *Bitumen* **6,** 49 (1936); Oberdach *ibid.*, **5,** 137 (1935); Kadmer, *Seifensieder-Ztg.*, **62,** 813 (1935); Smith, *J. Inst. Engrs. Australia*, **7,** 361 (1935); Kirschbraun, *Eng. News-Rec.*, **114,** 276 (1935); Mack, *Ind. Eng. Chem.*, **27,** 1500 (1935).

[13] A wealth of material is contained in the *Proceedings of the World Petroleum Congress* (London, 1933), Sectional Volume " G " (1934). See also: McKesson, *Proc. Am. Soc. Testing Materials*, **84,** 1–10 (1931); Temme, *Asphalt Teer Strassenbautech.*, **33,** 457, 477 (1933); Mallison, *ibid.*, **32,** 229 (1932); Keppler and Dohse, *ibid.*, **32,** 939 (1932); Neubronner, *ibid.*, **32,** 393 (1932); Vallé-Jones, *Munic. Eng. Sanit. Record*, **81,** 623 (1928); Wieland, *Bitumen*, **2,** 113 (1932); Steinitz, *Petroleum Z.*, **29** (xxi), 6 (1933); Oberbach, *Teer. u. Bitumen*, **34,** 271 (1936); Jachzel, *Asphalt Teer Strassenbautech.*, **36,** 101 (1936); Kresse, *Bitumen*, **6,** 59 (1936); Riedel, *Asphalt Teer Strassenbautech.*, **36,** 119, 191 (1936); Herrmann, *ibid.*, **35,** 905 (1935); Mallison, *ibid.*, **35,** 884 (1935); Temme, **39,** 417 (1939); Vellinger, *Rev. petrolifere*, **828,** 344 (1939).

directed to the elementary problem of coagulation.[1] Thus, Myers[2] employed $CaCl_2$ and McKesson[3] details the test for quick-setting emulsions thus:

"One hundred grammes shall be placed in a tared 600 ml. glass beaker, and 35 ml. of 0·02 normal solution of calcium chloride shall be added during a period of approximately 2 minutes, being continually and vigorously stirred and the lumps kneaded against the sides of the beaker with a rounded and glass rod not less than $\frac{5}{16}$ in. diameter. The emulsion and calcium chloride solution shall be maintained at a temperature of approximately 77° F. during the time of adding the reagent and stirring. The contents of the beaker shall be drained through a 14-mesh iron wire sieve and the unbroken emulsified asphalt in the beaker and on the rod shall be rinsed through the sieve with distilled water. Lumps of asphalt shall be kneaded and broken up and the rinsing continued until there is no appreciable discoloration of the rinsing water. The beaker, rod and sieve shall then be dried in an oven at 163° C. for 3 hours and weighed. The percentage of asphalt residue deposited in the beaker and on the rod and sieve shall be taken to be the difference between the weight of the beaker, rod and sieve after drying and their tared weight determined at the beginning of the test."

McKesson states that many of the large users of bituminous emulsions in the United States specify a demulsibility by this test method of 60—80 per cent. He also points out that while quick setting and high demulsibility are required in emulsions intended for penetration or grouting, slow setting is required in those emulsions intended to be distributed as a coating over the surfaces of the aggregate before coalescence. In the latter case, Myers' test is modified: 100 grammes of emulsion are taken with 50 ml. of 0·1 N. $CaCl_2$. "To ensure proper mixing time and proper coating the demulsibility should not be more than 30 per cent. where coarse aggregate is to be used, not more than 5 per cent. where fine dusty aggregate is to be used."

Myers' test is empirical,[4] in the sense that it does not logically anticipate the action of the emulsion against various minerals. Confined to emulsions stabilised with alkali or soap, it probably gives a first quantitative measure of the normal stability of the emulsion, but it cannot justifiably be admitted in the cases where the emulsifying agents do not undergo metathesis with Ca ions. Smith[5] mentions that other factors than the formation of calcium soap are suggested by the rather pronounced temperature effect.

In connection with bitumen emulsions stabilised with potassium tannate alone or with potassium caseinate also present, Hixson and

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[1] Caroselli, *Bitumen*, **6**, 61 (1936); Korzhuev and Gridchina, *Colloid J.* (*U.S.S.R.*), **5**, 943 (1939).

[2] Described with an experimental survey by Smith, *Ind. Eng. Chem. Anal. Edn.*, **4**, 105 (1932).

[3] *Proc. World Petroleum Congress* (London, 1933), Sectional Vol. "G" (1934), p. 689. See also Neubronner, *Asphalt Teer Strassenbautech.*, **33**, 10 (1933).

[4] Clayton, *Proc. World Petroleum Congress* (London, 1933), Sectional Vol. "G" (1934), p. 691.

[5] *Ind. Eng. Chem. Anal. Edn.*, **4**, 105 (1932).

Fain[1] describe a demulsification test using ferrous sulphate solution. They found that an emulsion of Mexican asphalt, in the tannate solution to which subsequently was added the caseinate, gave no deposit on screening on the addition of $FeSO_4$, although such a deposit resulted with the emulsions stabilised with either tannate or caseinate alone.

BREAKING ON CONTACT WITH STONE

The major physico-chemical problem concerned in the use of bituminous emulsions as road dressings is that of the breaking or coagulation of the emulsion on contact with stones of various types.[2] Intimately connected with the same problem is the adhesiveness of the bitumen on stone, *i.e.*, its function as a binding agent. The investigation deals with the solid/liquid interface and wetting phenomena.

It is obvious that any tests devised to determine breaking of the emulsion should be carried out with the particular stone under consideration.[3] Stones react differently to different types of emulsions, but according to Suida and Uiberreiter[4] they may be roughly classified on the basis of their activity, which appears to parallel alkali adsorption of the stone. Deposition of bitumen due to water evaporation is greater the less active the stone. Accordingly, in dry warm weather the emulsion breaks due to this factor, while in cold wet weather the specific action of the stone controls the behaviour of the emulsion. Rick[5] believes the emulsifier remains dispersed in the bitumen after evaporation of the water as a filiform structure which can modify the elastic, thermal and ageing properties of the bitumen ; it is, however, too fine to diminish its water resistance.

The " breaking value " has been defined[6] as the quantity of bitumen precipitated from a given amount of emulsion by the action of gravel of a definite screen analysis. The results reached by this test with various minerals showed : (1) relative to the mineral constituent, the breaking value depends upon (*a*) the adsorption capacity of the mineral with respect to the alkali of the emulsion, and (*b*) the effective surface ; (2) relative to the emulsion, the breaking value is a function of (*a*) the content of alkali and emulsifying agent in the emulsion, (*b*) the sensitivity of the emulsifying agent towards alkali removal, (*c*) the bitumen content of the emulsion, (*d*) the softening point and the particle size of the emulsified bitumen.

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[1] *Ind. Eng. Chem.*, **24**, 1339 (1932).

[2] Important papers dealing with breaking are by : Thron, *Asphalt u. Teer*, **32,** 493 (1932) ; Wilhelmi, *ibid.*, **32,** 10 (1932) ; Kell, *Bitumen*, **3,** 11 (1933) ; Dahlberg, *Asphalt Teer Strassenbautech.*, **34,** 585 (1934) ; Klinkmann, *ibid.*, **33,** 842, 873, 893 (1933) ; Vandone, *Proc. World Petroleum Congress*, Sectional Vol. " G," 664 (1934) ; Weber, *ibid.*, p. 669 ; Geissler and Kleinert, *Asphalt Teer Strassenbautech.*, **35,** 1018 (1935) ; Kleinert, *ibid.*, **35,** 194 (1935) ; Klingmann, *Bitumen*, **5,** 206 (1935) ; Suida, Jekel and Haller, *Asphalt Teer Strassenbautech.*, **39,** 253 (1939) ; Nasini and Rossi, *IX Congr. intern. quim. pura aplicada*, **2,** 383 (1934) ; Winterkorn, *Assoc. Asphalt Paving Tech., Proc. Tech. Sessions*, **1936,** 79.

[3] The general problem of fillers and road mixes is dealt with by : Stanton and Pauls, *Public Roads*, **15,** 253 (1935) ; Neumann, *Gas World*, **102,** 95 (1935) ; Hubbard, *Proc. World Petroleum Congress*, Sectional Vol. " G," 601 (1934) ; Evans, *ibid.*, p. 608 ; Nellensteyn, *ibid.*, p. 616 ; Neumann and Wilhelmi, *ibid.*, p. 619.

[4] *Petroleum Z.*, **29,** No. 29, 1 (1933).

[5] *Teer u. Bitumen*, **32,** 113 (1934).

[6] Keppler, Blankenstein and Borchers, *Angew. Chem.*, **47,** 223 (1934).

Riedel[1] has conducted special investigations into the causes of adhesiveness of bituminous materials against stone. The changes in acid number of a light spindle oil containing naphthenic acids were noted in relation to contact with stones. With increasing water content of the stone the acid number decreases in basalt; for hydrophilic porphyry it is first unaffected, then attains a maximum and finally slowly decreases; for glass it decreases to a minimum, then increases slowly owing to emulsification of the oil with the water from the glass. That decrease in acid number is due to surface adsorption of polar molecules and not to chemical neutralisation is shown mathematically and by experiments with powdered porphyry and with Na_2CO_3. Differences in behaviour between hydrophilic and hydrophobic solids are explained by their different decreases in free surface energies in the adsorption of the naphthenic acid, a secondary reaction taking place in the hydrophobic surfaces.

The nature of the secondary reaction between polar molecules and stone surfaces was next investigated[2] by the same technique, the acidified oil being in contact with $MgCO_3$, $CaCO_3$, Fe_2O_3 and Al_2O_3. Unextractable (by C_6H_6, water and alcohol) soaps and salts of naphthenic acids adsorbed on stone surfaces were shown to be responsible for the acquired resistance to wetting, which was similar to that of Mg stearate adsorbed from oil. The wettability by acidified oil and water of many metals, salts and inorganic compounds was determined. Study of many minerals shows that those of acidic nature (greater molar content of acidic constituents) are hydrophilic, those of basic nature hydrophobic. Hydrophobic substances form compounds with the polar molecules of wetting liquids which are water-insoluble but soluble in the wetted phase. Hydrophilic substances either undergo no reaction with wetting liquids or form water soluble compounds therewith.

WEBER'S INVESTIGATIONS

Notable work has been carried out by Weber and his associates[3] on the breakdown of bituminous road-making emulsions in contact with stone. He rejects those tests which depend on dipping the stone in the emulsion for a short time to determine "breaking," or mixing the stone with the emulsion prior to drying to determine "sticking." Such tests, he asserts,[4] mainly involve evaporation of water and do not reflect the specific reactivity of the emulsion with the stone, which controls the coagulation of the emulsion in the interior of the moist road surface.

To investigate the mutual influence of the emulsion and the stone, Bechler and Weber quantitatively determine the breakdown of the emulsion in contact with stone by mixing with an excess of the emulsion a weighed amount of stone of definite grain size. Evaporation of water is prevented during the period of contact, at the end of which the unreacted emulsion is decanted off, the stone washed carefully with distilled water and then dried. The residual bitumen-stone agglomerate is then weighed.

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[1] *Asphalt Teer Strassenbautech.*, **34**, 429, 487 (1934).

[2] *Ibid.*, **34**, 924, 941, 961, 979 (1934).

[3] Weber and Bechler, *Asphalt Teer Strassenbautech.*, **32**, 45, 69, 95, 129, 149, 173 (1932); Riedel and Weber, *ibid.*, **33**, 677, 693, 713, 729, 749, 793, 809 (1933). Critical discussion of these papers is by Walther, *ibid.*, **33**, 698.

[4] Weber, *Ind. Chemist*, **9**, 240 (1933).

Such factors as grain size, cleanness, new or old cleavage, ratio of stone to emulsion, time of contact, temperature, method of washing off the excess emulsion, etc., were all investigated. The chosen grading is 0·6—2 mm., based on the fact that too large grains increase the experimental error due to irregularity in the surface exposed, whilst too fine grains prevent removal of the excess emulsion without loss of stone. Although washed and unwashed stone gave similar results, the authors recommend washed stone for the test. Newly-cleaved stone is about 60 per cent. less reactive than stored stone, as a rule. The laboratory test, therefore, uses freshly cleaved material so as to approximate road conditions of dressing. Temperature was observed to be without importance.

The authors report remarkable variations in the speed of breakdown of emulsion in contact with various stones, whilst individual emulsions showed the same marked variations in the rate of breaking against the same mineral. They mention, for example, that whilst the separation of bitumen in contact with a porphyry or limestone of a certain origin was not complete even after 48 hours, the same emulsion was completely broken in 1 hour in contact with a limestone from another deposit or a basalt. " The binder separated in the first case after 1 hour amounted to 10 times that separated in the 1 hour in the second case. After 2 days the amount had increased to 7 times that after 1 hour. In the second case the 1 hour value had not increased after 2 days. It is thus clear that combinations of emulsion and stone with little capacity for reaction generally show no appreciable separation of bitumen after considerable periods. In our opinion this observation is of great practical importance because it shows that if an emulsion is used which will break scarcely or not at all in contact with the stone of the road, no improvement in this condition is to be expected even after days and weeks, so that it will remain for long periods in the unbroken condition, *i.e.*, in a condition in which it is useless as a binder."

The important point is also emphasised that " the greatest similarity in the behaviour of two emulsions towards a series of stones does not allow of any conclusions being drawn as to their behaviour towards *all* stones." Again, aged and sedimented emulsions on reconstitution show the same original reactivity.

Weber believes his researches have shown that the breaking of the emulsion is not due to withdrawal of water by capillary penetration into the stone mass. It is, however, dependent on the amount of emulsifying agent in the emulsion, whether it be present as free alkali, alkali carbonate or soap. In this connection it is interesting to note that pretreatment of stone with alkali rendered the most active stones completely passive even to the most labile emulsions. Soap is less effective than alkali in this respect. Washing with water of a pretreated alkaline stone does not restore the activity of the stone.

THE MECHANISM OF BREAKING

Weber explains the mechanism of the breakdown of the emulsion on stone thus : " When the two materials come into contact with each other, the reactivity of the mineral with the emulsifier as present in emulsions which break with ordinary ease leads rapidly to such an impoverishment of emulsifier in the zone of contact between mineral and emulsion that the equilibrium of the emulsion is destroyed and the precipitation of bitumen commences. Products with considerably more than normal soap content therefore do not break, as with them the capacity for reaction of the stone becomes saturated before the reduction in the concentration of the emulsifier has gone far enough to endanger the stability of the emulsion. Pickering emulsions remain completely stable even in contact with highly-active stone, as this has no capacity for reacting with or adsorbing the solid stabiliser. The extent to which the breakdown of the emulsion progresses depends on the ease with which the mineral is wetted by the bitumen. If the wetting is easy, the spongy bitumen first precipitated soon flows together to form a dense skin of bitumen, and the breakdown of the emulsion comes to a standstill. The degree of weathering of the stone, and the presence or preponderance of certain minerals in it also play an important part. *The bitumen itself is primarily not concerned with the initiation of the breaking process.*"

It is interesting at this point to note the findings of Lorne [1] on the *adsorption of specific fractions* of bitumen by certain natural and treated earths, such as kieselguhr, Florida earth, activated bauxite and limestone. The efficiency of such fillers is not parallel to their decolorising properties (which is the usual factor explored in adsorption studies). The different earths adsorbed different fractions of low or high molecular weight.

Lee [2] has discussed the general characteristics of adhesives and of adhesive processes in their bearing on the problem of adhesion in relation to bituminous road materials, showing that the first attribute of an adhesive is that it should wet the solid on which it is placed. Thereafter it should change into a more or less solid tenacious material, bearing in mind that a treated road surface may be wetted by rain prior to setting of the ahdesive. He experimentally followed the displacement of tar and bitumen films by water, noting the improvement gained by the addition of fillers such as granite dust. Highly polished and water-wetted stones showed little differences in being wetted by tar. Lee states : " The difference found in practice with various types of stone must be due not so much to the specific chemical relations between the stone and binder as to the physical, mechanical, and geometric properties of the stone. This result should be considered in relation to the theory which attempts to explain adhesion phenomena in terms of the acidic or basic nature of the solid relative to the binder. Acidic stones are considered to give poorer adhesion than basic stones towards various road binders. Tests with polished marble and limestone, however, show that if the tar contains acidic constituents these will dissolve or hydrolyse in the water and cause chemical action by the resulting dissolution on the basic stone. In the absence of solution or hydrolysis there is no chemical action."

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[1] *J. Inst. Petroleum Tech.*, **22**, 541 (1936). See also Mack, *Ind. Eng. Chem.*, **27**, 1500 (1935), dealing with energy relations at the interface between asphalt and mineral aggregate.

[2] *J. Soc. Chem. Ind.*, **55**, 23 T. (1936).

The conclusion was reached that surface texture and moisture content appear to be the predominating properties of the stones commonly used in road construction. Tar adhesion even after 24 hours immersion in water was obtained if the stones were treated in advance with oil (crude fluxing creosote oil) and weathered by outdoor exposure.

Winterkorn and Eckert[1] have pointed out that whilst wetting phenomena are usually instantaneous, the development of maximum adhesion between a mineral surface and bituminous material is a function of time. They examined McLeod's application of flotation principles to the problem of bitumen adhesion[2] by experiments with silica sand, concluding that simple mixing is not a dependable measure of the adhesion. A wash test is preferred.

MODERN PERFORMANCE TESTS

The present tendency is to devise for laboratory use some performance test which will take into account the many factors involved in the first history of bitumen applied to a road and will approximate to subsequent road conditions. Thus, Mack[3] has described two machines as affording practical means of studying the problem of adhesion and the effect of traffic. He notes the following factors bearing on the stability of a bituminous pavement in the presence of water : temperature ; adhesion of bitumen to aggregate ; speed of the wheel ; amount and distribution of traffic ; surface contour of the pavement ; scuffing action of the wheel. Other factors yet open to investigation are : load ; variation in rest periods ; change in physico-chemical properties of bitumens due to oxidation on the road ; change of colloidal properties of bitumens due to ageing ; type and mechanical properties of pavement.

Mack found that heavy-metal soaps (such as lead acetate-naphthenate) reduced the interfacial energy between bitumen and aggregate and increased the interfacial energy between bitumen and water. Since the data presented (number of revolutions of wheel for failure) showed the remarkable effect of small amounts of lead soaps in stabilising the treated track, it is clear that Mack has opened up a new line of attack on the problem. Suitable double salts of heavy metals containing organic acid radicals of low and high molecular weight permit a base-exchange reaction. Thus, with lead acetate-naphthenate, the base-exchange occurs through the acetic acid radical, whereby the lead is anchored with one valency in the surface of the aggregate and orienting the hydrophobic part of the naphthenic acid radical towards the bitumen.

A thorough discussion of performance tests has been presented by Gabriel and Peard[4] who dismiss Myers' test as resting on unwarrantable assumptions and with this the present writer concurs. They point out the futility of making tests involving the reaction of the emulsion to one particular factor inducing breakdown. Their own tests are "imitative" of road conditions. The time elapsing after applying emulsion is important since "setting" and "binding" are successive events. The former process takes place after application so that the bitumen particles join up to form a coagulum. The latter process may follow or may not, although setting has taken place.

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[1] *Ind. Eng. Chem. Anal. Edn.*, **11**, 546 (1939).

[2] *Assoc. Asphalt Paving Tech., Proc. Tech. Sessions*, **1937**, 1–62.

[3] *J. Soc. Chem. Ind.*, **60**, 111 T. (1941).

[4] *Ibid.*, **60**, 78 T. (1941).

The authors' two tests are (1) a model road test with wheels arranged on a revolving arm and a track with the surface in sectors so that several tests could be run simultaneously, the loosening of stone chippings providing the quantitative basis of the test; (2) the setting performance test, the principle being "to prepare a test surface similar to an actual road surface, to apply to this the emulsion under test, to bind it with chippings, to allow it to set for suitable periods of time, and then to apply a disintegrating force by stroking with a specially constructed comb-tool."

Three main factors are recognised as producing the set of emulsion on the road: (1) evaporation; (2) lability; (3) coagulative effect of stone aggregate. The abrupt change in the rate of evaporation of water from an emulsion film can be identified with lability point if the drying conditions include mechanical disturbance. "The lability number itself does not give a measure of the time taken for the emulsion to set; it merely defines the composition of the emulsion when coagulation is well advanced. If a measure of the setting time is to be obtained, cognisance must be taken of the original composition of the emulsion."

Gabriel and Peard developed a new stone coagulation test after noting the defects of Weber and Bechler's test. Reproducible coagulation was the aim. It was accepted that alkali and soap adsorption occurred from aqueous solution of the emulsifier by the stone, but the process was a function of time of contact, ratio of stone surface area to amount of emulsion used, and the precise conditions of mixing. The procedure finally adopted was to place chippings of practical size in contact with a film of emulsion, as distinct from the hitherto usual methods of immersion. The authors' description of the new test is quoted.

"The apparatus required for the test consists of (*a*) a glass tray 25 cm. × 25 cm. area with ½-in. angle-iron rim attached by glycerin-litharge cement and fitted with an air-tight glass coverplate; (*b*) flat-bottom nickel dishes 8·5 cm. diameter and 1·5 cm. deep. The aggregate is graded ¼ in.–⅜ in., washed, and air-dried. The glass tray is accurately levelled and coated evenly with 60 c.c. of emulsion, 450 grm. of aggregate are spread rapidly on the emulsion film, the tray is covered to prevent evaporation, and emulsion and aggregate are left in contact for 4 hours. After this period, the residual emulsion is washed out with distilled water, avoiding as far as possible any mechanical disturbance of the aggregate. Emulsion and washings are passed through a 25-mesh sieve, and the sieve residue and bitumen remaining on the tray and aggregate extracted by xylene. The xylene solution is filtered, made up to 1 litre, and the quantity of coagulated bitumen estimated by evaporating 25 c.c. portions of the solution in the nickel dishes. During the evaporation, standard conditions must be maintained, the dishes being placed for 1½ hours on the water-bath, not in direct contact with the steam. The coagulation value is expressed as the percentage of bitumen coagulated, calculated on the total bitumen present."

Interesting data are recorded by the authors and they state that there is no relation between Myers' test and performance, measured by either of their two methods.

PATENTS DEALING WITH BREAKING

A number of patents relate to special methods of treating the bituminous emulsions with regard to breaking on contact with the road. Plasticity of the bitumen is claimed by the use of a solvent such as benzene present in the aqueous external phase of the emulsion.[1] Facilitated spreading is gained by treating the aggregate or road surface with solutions of pyridine or pyridine bases or by adding such solutions to the emulsions.[2] The addition of a fine aqueous suspension of coal-tar pitch to the emulsion is stated to facilitate breaking down of the mixture and the formation of a hard coherent layer on the road.[3]

Several patents mention the use of electrolytes to cause rapid breakdown of the emulsion. Thus, dilute solutions of salts of metals such as Al, Fe or Ca are incorporated in a mixture of mineral aggregate and bituminous emulsions to aid rapid separation of the bitumen.[4] The addition may be to the aggregate or to the road before emulsion application or the solution may be applied after spraying the roads. Limburg [5] claims a process in which the aqueous bitumen emulsion is mixed with an aqueous volatile reagent such as ammonia and with a potential coagulant brought to active coagulating condition upon evaporation of the volatile alkali. The treated emulsion is applied as a film to the road and the volatile alkali is permitted to evaporate from the film to accelerate coalescence of the bitumen particles before complete removal of water from the film. Fabre [6] coagulates the bitumen with $CaCl_2$ and Gough [7] claims the use of demulsifying agents. Roads may be treated with alum solution [8] or with a mixture of $NaHSO_4$ and H_2SO_4.[9] Mineral or other aggregate may be coated with bitumen by applying it in the form of an emulsion with a small quantity of a salt such as NaCl or Na_2SO_4, a filler such as soft limestone being added to absorb water set free from the emulsion.[10]

The claim is also made of using an unstable emulsion free from emulsifier.[11] Again, fine material is removed from road metal and the coarse sprayed with the bitumen emulsion while being gently tumbled so as not to break the emulsion. The fines are then sprayed on with such violence as to break the emulsion and cause a film of bitumen to form on the coarse particles.[1] Another idea [2] is to make a mixture of emulsions, one of relatively coarse grain, bulk instability and quick-breaking character, the other a finer, stabilising system. Quick adhesivity by using aggregate heated to 250° F. is claimed by Watts.[3]

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[1] N. V. Mijnbouw-en Cultuur Maatschappij " Boeton," Fr. 670,570 (1929).

[2] Fox, Brit. 332,897 (1929).

[3] Burt, Boulton and Haywood, Ltd., and China, Brit. 316,780 (1928).

[4] Berry, Wiggins & Co., Ltd., and Holmes, Brit. 322,923 (1929).

[5] U.S. 1,984,024 (1934).

[6] Fr. 664,563 (1928).

[7] Brit. 312,467 (1928).

[8] Carson, U.S. 1,960,865 (1924).

[9] Mumford and Butterwork, Brit. 233,826 (1924).

[10] Colas Products Ltd., Whiting and Terry, Brit. 301,544 (1927).

[11] Plauson, U.S. 1,949,876 (1934).

SOIL STABILISATION

Within the past decade marked consideration has been given to the subject of oil stabilisation, which terms refers [4] to the change in soil characteristics in which the capillarity of the soil and its affinity for water are reduced to a point which will ensure required bearing strength in the soil under actual conditions of exposure in the subgrade. A wide literature is accumulating.[5]

Lawrence [6] has recently reviewed the problem and his paper and that of Thurston and Weetman [7] should be consulted for details.

The stabilisation of soil may be in part secured by controlled grading and by the use of such chemical compounds as calcium chloride,[8] which maintain the moisture content of the soil at an optimum (maximum strength of the soil). However, such stabilisation without waterproofing is passing in favour of the waterproofing method, as by treatment with bitumen emulsion.

Of the fractions concerned in soil analysis it is the clay which is important, this being the fraction passing the 200-mesh sieve. It is the active and colloidal fraction, holding water by imbibition, being plastic when sufficiently swollen and exhibiting pronounced differential in volume according to its state of dryness. Its cohesive action on the soil is a notable feature, but excess water negatives this action, so that the soil is easily deformed and displaced by a load. Correct treatment with a suitable bitumen emulsion gives a clay bearing soil a marked resistance to capillary water. It is not economical to render soil completely waterproof, and it suffices to add enough bitumen to make certain that the treated soil will no longer absorb water to render the soil unstable and unable to carry a load.

The laboratory examination of soils prior to deciding the appropriate bitumen treatment determines the *liquid limit* (percentage of water required to be mixed with oven-dried soil to effect free flowing) and the *plastic limit* (the lowest moisture content, in percentage of the oven-dried soil, at which the soil may be rolled into threads $\frac{1}{8}$ in. diameter without the threads breaking). For both tests the soil is the fraction passing 36 mesh.

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[1] Loomis, U.S. 1,911,761 (1933).

[2] Colas Roads Inc., U.S. 1,894,617 (1933). See Brit. 362,577 (1930).

[3] Can. 356,608 (1936).

[4] McKesson, *Can. Engr.*, **70** (vi), 5 (1936).

[5] Hogentogler, *ibid.*, **71** (xi), 43 (1936); Flinn, *ibid.*, **73** (xii), 136 (1937); Morton, *Agr. Eng.*, **19**, 475 (1938); Gray, *Military Engr.*, **31**, 99 (1939); a series of papers in *Proc. Highway Research Board*, **18**, 11 (1938), and by Mills, Scoggin, Loughborough *et al.* in *ibid.*, **19**, 491–516 (1939); Garneau, *Eng. Contract Record*, **54** (ii), 20 (1941).

[6] *J. Inst. Petroleum*, **26**, 357 (1940).

[7] *Assoc. Asphalt Paving Tech., Proc. Tech. Sessions*, **1939**, 37.

[8] Moreland, *Proc. Highway Research Board*, **19**, 563 (1939); see also several papers in *ibid.*, **18** (1938), by Wilford *et al.*

Should the clay fraction exceed about 30 per cent. the emulsion treatment is not economical. To determine whether satisfactory stabilisation is possible with bitumen emulsion, cylinders are prepared and tested for capillary water absorption by standing them on a wet base for a definite time. Thereafter the samples are compressed and the maximum load noted just before cracking. Although an untreated soil will not stand much in excess of 15 lb. per square inch, a properly stabilised soil after exposure to the water absorption test will withstand a pressure of 250 lb. per square inch. The normal quantity of emulsion required is from 6 to 10 per cent. by weight of the soil fraction, exclusive of stone.

The practical details of surface treatment[1] are beyond the scope of this volume. An interesting account of the stabilisation of soils for runways on aerodromes has been presented by Haswell.[2]

EMULSIONS IN THE LEATHER INDUSTRY

Following the tanning of skins to form leather, it is usual to incorporate oil or fat in order to lubricate the fibres, thus making the leather soft and pliable.[3] If the oil or fat is employed direct, the operation is termed *stuffing*, whilst if an emulsion is used, the operation is termed *fat-liquoring*.[4] A wide variety of animal and vegetable oils and fats is used, whilst in fat-liquoring sulphonated oils are prominent.[5]

The previously-smoothed flesh side of the evenly-split leather is treated, sometimes, as with heavy leathers intended for beltings of harness, previously dried out.[6] Stuffing may be executed by hand or machine (drum stuffing). Optimum stuffing results when wet leather is oiled, as the unsaturated acids of the oily material apparently undergo oxidation under the influence of water to yield dihydroxy fatty acids which have a tanning action.[7]

The student of the physical chemistry of emulsions finds interest in the general inquiry into the factors involved in the adsorption and distribution of oil in leather which has been fat-liquored, and particularly in the influence thereon of the emulsifying agents employed. Although the skins may adsorb up to 20 per cent. of oils or fats, the distribution is by no means uniform. The main oil adsorption is not from the flesh side but through the grain. Several workers[1] have pointed out that the centre of a skin may be free from oil; in fact, an unlubricated middle stratum ensures firmness, a soft and raggy leather following oil adsorption to the centre strata.

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[1] Cf. International Bitumen Emulsions Ltd., Brit. 489,767 (1939).

[2] Technical Paper, No. 11, issued by the Engineer-in-Chief, Army Headquarters (New Delhi, 1934). See also " A Study of Roads and Aerodromes and the Uses of Emulsified Asphalt in America in 1933," by Haswell. (Quetta—the Albert Press).

[3] Full technical details are described by Wilson, " The Chemistry of Leather Manufacture " (New York, 1929), Vol. 2, Chaps. 27—29. Schindler, " Die Grundlagen des Fettlickerns " (Leupzig, 1928) treats the underlying principles in considerable detail. See also Wilson and Gallun, *Ind. Eng. Chem.*, **16**, 1147 (1924) on the subject : " Strength and Stretch of Calf and Kid Leathers as Functions of Oil Content."

[4] See Kohnstein, *Seife*, **6**, 532, 568 (1921) ; Stiasny, *Collegium*, **1928**, 230 ; Arnold, *ibid.*, **1928**, 292 ; Prien, *ibid.*, **1932**, 580 ; Auerbach, *Ledertech. Rundschau.*, **20**, 215 (1928) ; Thuau, *ibid.*, **7**, 81 (1915) ; Claflin, *J. Am. Leather Chem. Assocn.*, **25**, 544 (1930) ; Meunier, *J. Soc. Leather Trades Chem.*, **13**, 309 (1929) ; *Cuir tech.*, **18**, 64, 88 (1929) ; Geronazzo, *Boll. ufficiale staz. sper. ind. pelli mat. concianti*, **11**, 320 (1933). Detailed accounts are given by : Atkin and Thompson, " Technical Aspects of Emulsions " (London, 1935), Section 10 ; Dean, " Utilization of Fats " (London, 1938), pp. 257–282.

[5] Böhme, *Ledertech. Rundschau.*, **19**, 57 (1927) ; see criticism of this paper by Stadler, *ibid.*, **19**, 74 (1927) ; Schindler, *Collegium*, **1927**, 288 ; Bumcke, *J. Am. Leather Chem. Assocn.*, **22**, 621 (1927) ; Woodroffe and Crane, *J. Soc. Leather Trades Chem.*, **12**, 419 (1928).

[6] See Pollak, *Gerber*, **59**, 80, 89, 100 (1933).

[7] Cf. Moeller, *Gerber*, **45**, 277 (1919) ; *Collegium*, **1919**, 61.

Merrill[2] has reported quantitative experiments on fat-liquoring using sulphonated neatsfoot oil emulsions (water = 22·3; ash = 4·7; total oil = 73·0; SO_3 combined with oil = 3·4 per cent.). Borax or Na_2CO_3 was used to adjust the *p*H value. The leather employed was I-bath chrome calf, and tests were carried out at 40° C. His results on the distribution of oil in the skin show that :—

(1) For constant volume of emulsion, increasing the ratio : $\frac{\text{oil}}{\text{leather}}$, the amount of oil adsorbed increases linearly with the oil content of the emulsion.

(2) When the ratio $\frac{\text{oil}}{\text{leather}}$ is constant, the amount of oil taken up diminishes as the fat emulsion is diluted.

(3) Oil adsorption in the leather increases with times of immersion up to 4 hours and then remains constant. It seems that an equilibrium is established between the oil in the leather and that residual in the emulsion.

(4) A shift in the *p*H value of the emulsion or of the leather does not appreciably affect the total oil adsorption, but increasing the *p*H value enhances the penetration of oil into the skin.

Theis and Hunt[3] obtained characteristic fat-adsorption curves for various oils used in the fat-liquoring of chrome leather. Enumerating the variables stated by Wilson to influence the peculiarities witnessed in the far-liquoring of skins, they state :—

(1) The degree of disperson and stability of the emulsion are important, a very unstable emulsion leading to oil deposition on the surface of the leather, whilst a fine emulsion yields a very pliable leather, accompanied, however, by a looseness, especially in the flanks.

(2) The adsorption of oil from an emulsion by leather is not linearly related to the amount of oil in the emulsion.

(3) Oil adsorption increases up to about 4 hours, but penetration is hindered by deposition of oil in the surface layers.

(4) The adsorption of oil is not markedly influenced by the *p*H value of the emulsion.

Theis and Hunt questioned the influence of the *p*H value of the fat liquor. Pieces of shaved chrome skin were soaked to the desired *p*H value and then immersed in fat liquors for 1 hour at 38° C. Two types of emulsion were used: (A) sulphonated oil/raw oil. (B) sulphonated oil/raw oil/triethanolamine. Again, variations in the *p*H value of the emulsions were investigated.

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[1] Balderston, *J. Am. Leather Chem. Assocn.*, **17**, 405 (1922); Wilson, *ibid.*, **22**, 559 (1927); Merrill, *Ind. Eng. Chem.*, **20**, 181 (1928).

[2] *Ind. Eng. Chem.*, **20**, 181 (1928).

[3] *Ibid.*, **23**, 50 (1931).

It was observed that when the *p*H value of the skin was the variable, the amount of oil adsorbed increased continually from *p*H 1 to *p*H 4, thereafter greatly decreasing. An alkaline skin adsorbs less oil from the emulsion. At *p*H values < 5, the skin possessed a greasy feel, as though the oil had precipitated upon the outside fibres. At *p*H > 5, however, the skin possessed a soft, silky feel. The skin at *p*H values of 7 to 9 was well lubricated and from physical characteristics appeared to be well fat-liquored. With the emulsion containing triethanolamine (better oil dispersion), less oil is adsorbed and yet greater pliability results, whilst at *p*H 1 to *p*H 2, more oil is adsorbed and less detannising occurs.

For skins at constant *p*H value, immersion in fat liquors of different *p*H values gives quite different results to the above. With emulsion A, the oil adsorption gradually increases in the *p*H range 3 to 7, increasing more rapidly to *p*H 10, when a sharp decrease occurs, accompanied by a change in the leather from a pliable to a rubbery condition. With emulsion B more oil is adsorbed over the whole *p*H range than with emulsion A, the increase being steady to *p*H 10, when it drops rapidly. It was further found that different technical fat liquors possessed individual characteristic adsorption behaviour in relation to the *p*H value of the emulsion. Thus, for the system: raw neatsfoot oil/sulphonated neatsfoot oil, the oil adsorption over the *p*H range 3 to 7 is nearly uniform, but at *p*H > 7 the oil adsorption gradually increases, as does also the pliability of the leather. A marked decrease in oil adsorption occurs at *p*H > 10. In the case of a moellon fat liquor (oil residues from cod-liver oil tanning containing oxidised fatty acids) no oil adsorption occurs in the *p*H range 1 to 4, but from *p*H 4 to 5 a definite increase is noted. From *p*H 6 to 9 the adsorption is constant, falling sharply at *p*H 10. With sulphonated cod-liver oil, the adsorption is gradual over the *p*H range 1 to 9, when a sharp decrease occurs. Sulphonated cod-liver oil exhibits the greatest adsorption of all the fat liquors used over the *p*H range 1 to 5. Moellon shows the greatest oil adsorption in the *p*H range 6 to 8.

In a later communication [1] Theis and Hunt extended their experimental work to include the effects of: (*a*) mixtures of raw and sulphonated oils in relation to the adsorption of oil and the final strength of the leather; (*b*) moisture in the leather prior to fat-liquoring in relation to these same points; (*c*) mixtures of different oils upon the oil adsorption, strength of the leather and the distribution of oil throughout the skin.

As before, chrome-tanned calfskin was used, fat-liquored at 49° C. for thirty minutes. Employing mixtures of raw and sulphonated oils, variation was noted both in the oil adsorption and in the strength of the leather. Thus, whilst little oil adsorption occurs with raw neatsfoot oil, the oil adsorption progressively follows the incorporation in the emulsion of sulphonated neatsfoot oil. The strength of the leather, however, passes through a maximum at about 50 per cent. sulphonated oil. With 100 per cent. sulphonated oil, the strength of the leather is decidedly inferior to that resulting from the use of all raw oil, indicating thereby that the final strength of the leather cannot be gauged from the amount of actual oil adsorption.

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[1] *Ind. Eng. Chem.*, **24**, 799 (1932).

The temperature of the emulsion plays a *rôle*, the oil adsorption increasing over the range 21·1° C. to 48·9° C. and then decreasing with higher temperatures. The maximum strength of the leather developed when fat-liquoring took place at 26·7° C.

An important effect in oil adsorption is attributable to the presence of emulsifying agent, and Fig. 47 is reproduced from the authors' paper in this connection. The presence of an emulsifying agent results in enhanced adsorption of oil and greater strength of the leather.[1]

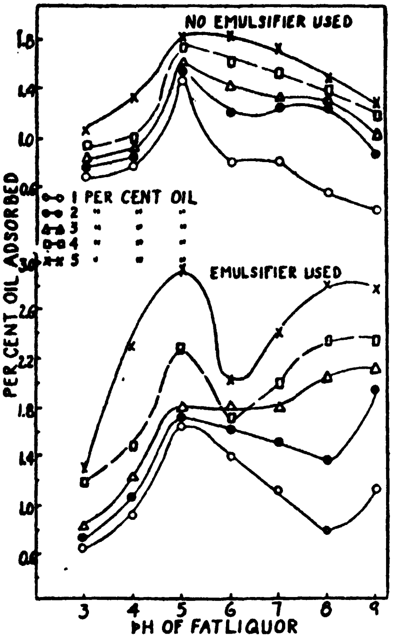

FIG. 47. Oil adsorption from fat liquors with and without emulsifying agent (Theis and Hunt).

Regarding moisture in the calfskin, it was found that with raw oils + emulsifying agent, oil adsorption was poorer the greater the moisture present; with sulphonated oils + emulsifying agent, the reverse is true, apparently due to the ready dispersion of the sulphonated oil in the water present in the skin.

The *rôle* of the chemical constituents of sulphated oils in the fat liquoring of chrome leather has been examined by Koppenhoefer and Retzsch[2] working with commercial sulphated neatsfoot, cod-liver and castor oils. Varying the constituents with regard to raw oil, sulpho compounds, free fatty acids and neutral oil in eleven series of tests, results were observed with the bend portion of commercial chrome-tanned calfskin, cut into strips after tanning, washed and neutralised with sodium carbonate. The extensive report should be consulted. *Inter alia* it was concluded that penetration through the grain surface is determined by the fineness of the emulsion and the sulpho compounds are incapable of lubricating leather, serving merely as dispersing agents.

A further paper by Koppenhoefer and Roddy[3] concerned the histological investigation of the fat-liquoring process. Pieces of chrome-tanned calf leather were fat liquored with a commercial sulphated neatsfoot oil, with a mechanical emulsion of neutral oil and free fat acids, with the sulphated compounds, and with various mixtures. Using pure

[1] Cf. also Schindler, *Collegium*, **1928**, 12, 241.
[2] *J. Am. Leather Chem. Assoc.*, **35**, 78–129 (1940).
[3] *Ibid.*, **35**, 317–330 (1940).

sulphated compounds, penetration was effected equally from the grain and from the flesh side. As the proportion of neutral oil increased, the proportion of oil absorbed through the flesh side increased. Neutral oil penetrated to a greater depth than the sulphated compounds, probably by migration on drying. The depth of penetration of the neutral oil increased with the total neutral oil absorbed, and also when the dry leather was flexed.

An important and extensively-used emulsifying agent in fat-liquors is egg or egg yolk.[1] Wilson[2] investigated the relative efficiencies of egg and its constituents in stabilising an emulsion system containing 5 grm. neutral and 5 grm. sulphonated neatsfoot oil in 100 c.c. The order of efficiency was : egg yolk > whole egg > egg white. Whole egg thickened by standing was found to be superior to fresh egg. Cobb and Hunt[3] point out that powdered egg yolk may be used dispersed in water adjusted with alkali to $pH = 8{\cdot}6$.

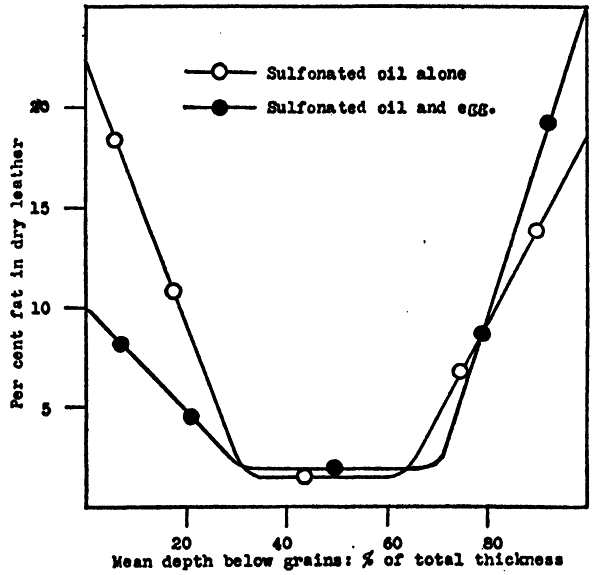

FIG. 48. Effect of egg yolk in the oiling of leather (Merrill).

Merrill,[4] working in Wilson's laboratory, has studied the effect of egg yolk on the distribution of oil in chrome calf leather. He states that the natural oil of egg is taken up by the skin and " it is highly probable that other constituents of the egg, including albumin and other proteins, and perhaps lecithin,[5] are likewise taken up, combining with the tanned fibres, increasing their bulk and generally adding to the substance of the leather."

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[1] Wilson, *Hide Leather*, **73**, 54 (1927) ; Hevesi, *Gerber*, **61**, 43 (1935) ; Leo and Cheng, *J. Chem. Eng. China*, **2**, 106 (1935) ; Oranienburger Chemische Fabrik A.-G., Ger. 607,609 (1935).

[2] *J. Am. Leather Chem. Assocn.*, **22**, 559 (1927).

[3] *Ibid.*, **21**, 18 (1926).

[4] *Ind. Eng. Chem.*, **20**, 654 (1928). See also *ibid.*, **21**, 364 (1929).

[5] Auerbach, *Gerber*, **55**, 209, 217 (1929), has proved the value of lecithin in fat-liquors. See also *Halle aux cuirs*, **1931**, 312.

One of the main advantages in the use of egg yolk is the increase in firmness especially of the loose portions of the skin. Again, the presence of egg yolk in a fat-liquor containing sulphonated neatsfoot oil alters the distribution of oil between the grain and flesh sides of the skin, the flesh side now adsorbing more oil than does the grain, thus improving the appearance of the finished leather.

Merrill treated 100-grm. samples of wet chrome calf leather with 50 c.c. portions of emulsion containing sulphonated neatsfoot oil and egg in varying amounts. Borax was employed to alter the *p*H value of the emulsion over the range 7·5 to 8·5 at the onset, the emulsion finally possessing a *p*H value in the range 6 to 6·5. Fig. 48 shows the effect of egg yolk in the emulsion on the distribution of oil in the leather, whilst Table 42 from Merrill's publication summarises the data obtained.

TABLE 42

EFFECT OF EGG YOLK IN FAT-LIQUOR ON THE DISTRIBUTION OF OIL IN CHROME CALF LEATHER

Number.	Sulphonated Neatsfoot Oil.				Oil in Whole Leather.	Total Oil in		Ratio G : F.
	Water.	Egg.		Borax.		Grain.	Flesh.	
	C.c.	Grams per 100 Grm. Wet Leather.			Per cent.	Per cent.		
			Egg variable.					
1	50	0	1·5	0·25	4·26	30	18	1·67
		2			4·85	19	16	1·19
		4			5·78	21	29	0·72
		8			6·52	14	32	0·44
			Sulphonated Neatsfoot Oil Variable.					
1	50	5	0	0·25	3·66	18	18·3	0·98
2			1·0		5·70	16	22	0·73
3			2·0		11·28	9	24	0·39
4			4·0		13·68	12	20	0·59
			Egg and Sulphonated Neatsfoot Oil Variable ·total oil = 1·7 grm.					
1	50	0	2·33	0·25	7·00	22	18	1·22
2		4·2	1·75		5·79	23	22	1·04
3		9·7	1·00		7·14	13	29	0·45
4		17·0	0		7·15	11	28	0·39

In the above table, in the first two sets of tests, commercial salted whole egg (10 per cent. fat) was used; in the last set the egg was unsalted. The sulphonated neatsfoot oil contained 76 per cent. total oil. The grain and flesh columns refer to 10 per cent. in each case of the total thickness of the skin, whilst the ratio G : F refers to the per cent. total oil in the grain and the flesh respectively.

To ascertain the effect of different egg constituents on the distribution of oil, Merrill used a fat-liquor containing 50 c.c. water, 2·5 grm. sulphonated neatsfoot oil, variable egg and 0·25 grm. borax per 100 grm. of wet leather. The following data were obtained.

TABLE 43

EFFECT OF DIFFERENT EGG CONSTITUENTS ON THE DISTRIBUTION OF OIL

Form of Egg.	Egg per 100 Grm. Wet Leather.	Ratio G : F.
None	None	2·19
Dried albumin	0·9 grm. (dry)	1·37
Fresh white	5	0·36
Fresh yolk	5	0·49
Fresh whole egg	5	0·65

"The addition of egg to the sulphonated oil emulsion causes an enormous increase in the size of the droplets." On this basis Merrill attributes difficulty in penetrating the small openings in the grain surface which consists of closely interwoven fibrils.

According to Theis and Hunt[1] the addition of egg yolk to a sulphonated neatsfoot oil emulsion does not always result in an increase in the total oil adsorption ; the *p*H value of the emulsion is an important factor. Over the *p*H range 1 to 4·5 the total oil adsorption is much below that adsorbed from a similar emulsion devoid of egg yolk. On the other hand, at $p\text{H} > 4{\cdot}5$, the adsorption of oil is greater from the emulsion containing yolk until the $p\text{H} = 6{\cdot}75$, whereupon the adsorption of oil again falls much below that obtained when yolk is not used. In other words, each emulsion, in relation to the *p*H value, has its specially characteristic behaviour.

Further, Theis and Graham[2] have investigated the distribution of free and combined oil in chrome leather layers. Henry,[3] discussing the factors affecting the distribution of oil in fat-liquored chrome leather, used cod-liver oil of three different stages of sulphonation and observed that the total oil adsorption was independent of the degree of sulphonation of the oil. Sulphonated compounds (acetone-soluble) and non-sulphonated (soluble in petroleum ether) were adsorbed in proportion to their concentrations in the oil used. Penetration was greatest for the oil of lowest degree of sulphonation and for non-sulphonated as opposed to sulphonated components.

Theis and Graham, however, found that when the percentage of sulphonated oils in the fat-liquors was low, the grain took up the oil, but as the percentage of sulphonated oil increased the flesh side exhibited a preferential adsorption of oil. Their results indicate "that low percentages of sulphonated oil give the greatest total oil content, while large percentages of sulphonated oil give the greatest combined oil value and correspondingly low values of free oil." Mellowing of leather for two weeks results in combination of the oil with the skin fibre or with the chromium nucleus. This is true particularly of the sulphonated or polar groups of the oil.[1] The authors conclude that each mixture of a sulphonated oil with a raw oil yields a new and different type of fat-liquoring as regards the distribution of free and combined oil. On the other hand, Merrill[2] believes that the difference in distribution between sulphonated and raw neatsfoot oil is so slight as to render it doubtful when binding of sulphonated oil at the surface can be considered evidence for union between the sulpho group and the chromium nucleus. (Reference should now be made to an interesting paper by Theis and Serfass[3] under the title: "Photomicrographical Studies of the Fatliquoring of Leather.")

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[1] *Ind. Eng. Chem.*, **23**, 52 (1931).
[2] *Ibid.*, **26**, 893 (1934).
[3] *J. Am. Leather Chem. Assocn.*, **29**, 66 (1934).

Phillips[4] emphasises that fats which wet leather easily are those which form orientated films on the surface of the fibres. In this way the oil is able to penetrate the interfibrillar spaces. The presence of water aids fat penetration by enlarging the channels between the fibres, providing the fat forms an oriented film on water.

A thorough discussion of the oiling of leather has been given by Rochow,[5] who summarises previous work. He outlines a simple theory of the mechanism of oiling leather on the basis that to lubricate the swollen fibres and fibrils they must be separated, and this is what the water phase must accomplish. Adsorption of the oil is then possible even by the tiniest fibres because they are *preferentially wetted by oil.* "All the other processes are necessary to reduce the surface tension of the oil in order that it may present a greater surface."

As to the actual mechanism of the penetration of oil into leather during fatliquoring, two recent papers hold much interest. Explanation is necessary of two facts: (1) the breaking of the emulsion in order that the oil globules form a film coating the surfaces of the leather fibrils, and (2) the mechanism of penetration of oil from the emulsion liquor into the leather interior.

Marriott[6] believes that the emulsion must break just inside the surface of the leather. He says:

"If one considers firstly the penetration from the flesh side of the skin it is easy to visualise the small globules of oil entering the somewhat large openings between the fibres and proceeding some small distance into the leather before reaching a position where the channel becomes too narrow for the globule to proceed any further. One does not, however, obtain in practice emulsions with globules so small that they can travel along the fine interfibrillary spaces. The packing of the fibrils into the fibres is far too close to permit any progress of oil globules. It follows therefore that the taking up of the oil is a surface effect and not a simple progression of tiny oil globules into the interior of the leather. A consideration of the structure of the grain layer and surface shows still more conclusively the utter impossibility of the entrance of globules of oil, since the grain surface is quite impervious, not only to globules, but even to large molecules. Even though the hair follicles might be considered as a possible means of entrance, it must be remembered that these structures are lined with the same tissues as the surface layer of the skin, and although at the base of the follicle where the capillaries which feed the root of the hair in life have left a break in the lining, the tremendous rate at which the globules would have to travel along the follicles and then finally meet the extremely close network of fine fibres of the grain layer entirely precludes this possibility."

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[1] Theis and Graham, *Ind. Eng. Chem.*, **26**, 743 (1934).
[2] *J. Am. Leather Chem. Assocn.*, **27**, 201 (1932).
[3] *Ibid.*, **31**, 120 (1936).
[4] *Ibid.*, **29**, 124 (1933).
[5] *J. Phys. Chem.*, **33**, 1528 (1929).
[6] "Wetting and Detergency" (London, 1937), p. 85.

He considers that the oil penetrates by a spreading effect "The spreading of the oil through the interstices of the grain and the fibres of the flesh will be dependent, however, on the ability of the oil to spread over oil-contaminated surfaces. . . . These results indicate that with any given finite surface there is a limiting size of globule which will spread to give a film of extreme thinness. If the surface is contaminated to more than a certain extent spreading will not occur at all, while if the globule be less than the limiting size a very thin film can be produced. In fatliquoring operations, therefore, if the size of the oil particle which is precipitated on the surface of the leather is very small, rapid spreading will occur and the film will be thin enough to penetrate. . . ."

Referring to heavily fatliquored leathers, he says : "In most of these leathers microscopical examination will show the presence of tiny globules of oil making it appear almost as though the actual globules of the emulsion had passed into the interior. These globules are, however, produced from the oil film itself. Most oils after spreading on water form a film which breaks up into holes and eventually into a network. This network then breaks down, leaving the oil in the form of large numbers of extremely small globules. It is the breaking of this film which gives rise to the oil droplets found in heavily fatliquored leather."

This theory was challenged by Blockey, Spiers and Johnson[1] who undertook an investigation to ascertain whether oil globules in a fatliquor do penetrate into leather during fatliquoring. A microscopical examination of the fatliquored leather was made. The emulsion was prepared from mineral oil + sulphonated cod oil with an oil-soluble red dye. Some of the authors' conclusions are :—

(*a*) There is no reason to suppose that the globules have been formed inside the leathers by the breakdown of films as suggested by Marriott. There is evidence to suggest that the globules observed in the leathers pre-existed in the fatliquor, for

- (*a*) a fatliquor can be forced through a calf leather with grain without entirely breaking down, and
- (*b*) pigment particles of a size about 5μ, which are larger than most globules in a fatliquor emulsion, can penetrate chrome leather to some depth.

(*b*) It is difficult to say with certainty what is the route taken by the globules in penetrating the leather from the grain side. The heavier staining of the calf and the hide grain split round the hair follicles and the glands suggests that the globules penetrate to some extent into the grain layer through them. The darker staining of the grain membrane in contrast to the uniform paler staining of the remainder of the thermostat layer, together with the presence of globules throughout the grain layer in the case of flesh split, sheepskin and grain split, suggest that in these cases the globules have also penetrated directly through the grain membrane itself. This probably also occurs upon calf leather.

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[1] *J. Intern. Soc. Leather Trades Chem.*, **23**, 347 (1939).

(*c*) During the fatliquoring operation the fibres to some extent become coated with a layer of grease. It is not clear as to whether this coating is a continuous film or not; sometimes it appeared to consist of small globules very close to each other.

(*d*) During drying, oil globules visible in the wet leather disappear, showing that, at any rate, the large globules break down to form a coating on the fibres.

(*e*) It is probable that one mode of entry of the grease during fatliquoring is the carrying into the leather of individual globules of oil brought about by the mechanical action of drumming. At the same time penetration by spreading, as suggested by Marriott, may occur.

The present writer believes that a thorough study still remains of this oiling problem, using homogenised emulsions of determined size-frequency analysis. The nature of the emulsifying agent should be examined, and, in this connection, the important work by Balfe and Uryash[1] is suggestive in regard to the effect of interfacial tension. The possibility of producing emulsions *in situ* should be explored.

PATENTS RELATING TO LEATHER EMULSIONS

A variety of emulsions for the treatment of leather is listed in the patent literature, usually with reference to some particular emulsifying agent.

Röhm[2] claims the dispersion of oil by the use of glue (or glue degraded with acid or enzymes) together with carbohydrate such as gum tragacanth or starch. He also[3] mentions an emulsion of oil and a salt of glycerophosphoric acid, *e.g.*, the Na salt. Related to this last patent is the claim to use lecithin as the emulsifying agent,[4] the residues from the extraction of soya-bean phosphatides may be similarly employed.[5] Röhm[6] has another interesting emulsion of neatsfoot oil stabilised with freshly-precipitated $Al(OH)_3$. Another instance[7] of the use of solid emulsifier is that of colloidal clays such as bentonite, the *p*H of the emulsion being adjusted for optimum swelling of the leather. Fish roe reduced to paste has been claimed.[1]

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[1] *J. Intern. Soc. Leather Trades Chem.*, **23**, 347 (1939); Balfe, *Leather World*, **31**, 559 (1939).

[2] Brit. 353,846 (1929); Ger. 518,920 (1929).

[3] U.S. 1,891,363 (1932).

[4] Bollmann and Rewald, Ger. 514,399; 516,187/8 (1927); Rewald, *J. Intern. Soc. Leather Trades Chem.*, **19**, 220 (1935); Sell, Olsen and Kremers, *Ind. Eng. Chem.*, **27**, 1222 (1935); Bull and Frampton, *J. Am. Chem. Soc.*, **58**, 594 (1936).

[5] Hanseatische Muhlenwerke A.-G., and Rewald, Ger. 522,041 (1927).

[6] U.S. 1,751, 217 (1930).

[7] Progil (Soc. Anon.), Fr. 742,563 (1933).

It would be anticipated that sulphonated and phosphorated oils[2] would feature as fat-liquors in the patents granted. Kinney[3] also mentions oil-soluble sulphonic compounds from mineral oils treated with H_2SO_4, whilst Kroch and English[4] specify sulphonated vegetable oils such as tea-seed or peach-kernel oil, containing 85—95 per cent. of esters of unsaturated fatty acids and which are liquid down to temperatures of $-6°$ to $-25°$ C. Sulphonated alcohols,[5] *e.g.*, oleyl alcohol, give good emulsions.

Somerville[6] specifies neatsfoot oil in emulsion stabilised by diethyloctylamine-HCl or other tertiary or quarternary amine salts of the same type.

Methylcellulose has been claimed as emulsifier,[7] whilst for leather dressing a solution of a film-forming colloid in an organic solvent is emulsified in an aqueous solution of a hydroxyalkyl or mixed alkylhydroxyalkyl ether of cellulose.[8]

EDIBLE EMULSIONS

The food industry provides many instances of the employment of emulsions. The chief edible emulsions are, of course, milk and cream, salad dressings and mayonnaise and certain medicinal emulsions. Less familiar, perhaps, are emulsions of essential oils for flavouring purposes,[9] the emulsions being made transparent if desired.[10] The old-fashioned "Marylebone Cream" was a 50 per cent. emulsion of linseed for infants, but, as pointed out by Hampshire and Hawker,[11] this lacks vitamin A, and beef suet would be preferable as the oil phase. Cod-liver oil emulsions have been used for animal feeding,[12] whilst patents have been granted for special emulsions, such as molasses emulsified with shortening agents,[13] or special ingredients intended to be recoverable in the milk.[14] Emulsification of the fat in toffee and caramels is recommended,[15] lecithin being excellent for this purpose. It is stated[16] that the capacity for emulsification is increased if the lecithin be treated with H_2O_2.

The enormously increased oil/water interface present in emulsions introduces problems of rancidity. The possibility that vitamin A in cod-liver oil emulsions would diminish due to some similar influence has been negatived.[1] Butter, a solidified emulsion, aptly illustrates the extent of the interface created.

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[1] Ehrenreich, Brit. 284,707 (1927). Cf. Emmerich, Ger. 688,647 (1940).

[2] See Gressner, *Hide and Leather*, **88** (xv), 22 (1934).

[3] U.S. 1,655,868 (1928).

[4] U.S. 1,988,905 (1935).

[5] Deutsche Hydrierwerke A.-G., Ger. 565,057 (1930).

[6] U.S. 1,883,042 (1932).

[7] I. G. Farbenind. A.-G., Ger. 524,211 (1926).

[8] I. G. Farbenind. A.-G., Ger. 600,197 (1934); cf. H. Th. Böhme A.-G., Brit. 313,966 (1928).

[9] Plauson's (Parent Co.) Ltd., Brit. 184,534 (1921). See also Brit. 435,272 (1935).

[10] Whitmore and Linehan, *Ind. Eng. Chem.*, **21**, 878 (1929).

[11] *Pharm. J.*, **103**, 82 (1919).

[12] Brigl, *Fortschritte Landw.*, **2**, 586 (1927); Zaribnicky, *Wien tierärztl. Monatsschr.*, **20**, 494 (1933); Edin., *Kgl. Landtbruks.-Akd. Handl. Tids.*, **68**, 763 (1929).

[13] Duff and Dietrich, U.S. 1,931,892 (1933).

[14] Jena and Jena, Ger. 501,332 (1924).

[15] Jordan, U.S. 1,859,240 (1932).

[16] Bollmann, Brit. 356,384 (1929); Ger. 511,851 (1929).

Under the microscope butter is seen to contain numerous water globules, and Boysen,[2] in his study of the structure of butter as investigated by photomicrography through parallel and crossed Nicol prisms, gives the following data for the distribution of the water globules.

TABLE 44

WATER GLOBULES IN BUTTER

Average Diameter.	Number of Globules.
1·9μ	12,905,700 per c.c.
4·0	230,490 ,,
7·5	61,469 ,,
12·5	10,740 ,,
20·0	628 ,,
30·0	139 ,,
40·0	57 ,,
50·0	25 ,,
60·0	12 ,,
70·0	8 ,,
80·0	5 ,,
90·0	4 ,,

According to Storch,[3] a cubic millimetre of butter contains from 2—13 million water globules, having diameters less than 10μ, and from 4—6 thousand water globules, with diameters over 10μ. Rahn and Boysen[4] find that ordinarily butter contains 12—18 billion water globules per gram, the majority, amounting to approximately 7 per cent. of the moisture, being smaller than 15μ. About 2 per cent. of the moisture is present as globules of diameters 15 to 100μ, whilst the remaining 4 per cent. of moisture is present as globules larger than 100μ.

There are fat globules also in butter, and King[5] has published his analysis of the size-frequency of the fat-globules following his examination of 10 samples. Thus, the average grading of each 100 globules shows :—

Average Diameter.	Number of Globules.
2·6μ	8·45
3·9	49·55
5·2	33·80
6·5	6·95
7·8	0·85
9·1	0·275
10·4	0·125

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[1] Griffiths, Hilditch and Rae, *Analyst*, **58**, 65 (1933). See Janes, Grover and Quinn, *Proc. Soc. Exptl. Biol. Med.*, **30**, 516 (1933); Zernik, *Pharm. Ztg.*, **70**, 156 (1925); Valentin, *ibid.*, **76**, 1423 (1931); Caspe and Hadjopoulos, *Am. J. Pharm.*, **110**, 533 (1938).

[2] *Milchwirtschaft. Forsch.*, **4**, 1 (1927).

[3] *Beretning frå den Kgl. Vet. og Landbohöjskole Lab.*, **36**, 1 (1897). See also Palmer, *Colloid Symposium Monograph*, **1**, 410 (1923).

[4] *J. Bact.*, **15**, 30 (1928).

[5] *Milchwirtschaft. Forsch.*, **8**, 423 (1929).

Palmer[1] has calculated that the water/fat interface in 1 lb. of butter may equal 1,000 square metres, and King[2] finds that the major portion of the interface is related to the small water globules present. Mundinger[3] definitely connects the rancidity of butter with the extent of the aqueous phase.

MARGARINE

Margarine is a substitute for butter, certain animal and vegetable oils and fats replacing butterfat. The oils and fats are liqufied together in certain proportions depending on the quality of the margarine required, and then churned with sour milk to form an emulsion. This emulsion is rapidly cooled, either by means of a spray of ice-cold water under pressure, or by flowing on to well-cooled revolving drums. The product in each case is then worked up by suitable kneading machinery to the required butter consistency and texture.

A typical margarine has a fatty composition as follows :—

	Per cent.
Premier jus	15
Coconut oil	15
Palm-kernel oil	50
Ground-nut oil	10
Cotton-seed oil	10
	100

The mixture of oils and fats is melted and then intimately mixed with milk, which has previously been " ripened " or " soured " by inoculation with certain strains of lactic acid micro-organisms. In the case of margarine intended for bakers' use, milk is replaced by water.

The most essential factor in the production of a margarine of a butter-like texture is the preparation of a stable emulsion containing from 77 per cent. to 84 per cent. fat and 23 per cent. to 16 per cent. water (milk serum). The milk used is at a temperature of about 7° C., and the melted mixture of oils and fats at about 40° C. Before actually chilling the emulsion, its temperature is reduced to about 24° C., so that a thick custard-like emulsion ensues, of greatly enhanced stability. The greater stability is due to the viscosity of the system, and furnishes an instance where viscosity is desirable in emulsion preparation. The object of chilling the emulsion is to fix the fine-grained condition arrived at, whereby the desirable intimate and finely-divided mixture is maintained in the solid state. Any " breaking " of the emulsion would lead to the formation of unemulsified fat, whereby the texture of the final product would be unsatisfactory.

Since milk is an ingredient, the emulsion type expected is the O/W, easily obtained if the oil phase is slowly run into the aqueous phase with stirring. The subsequent working of the congealed emulsion

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[1] *Ind. Eng. Chem.*, **16**, 634 (1924).
[2] *Milchwirtschaft. Forsch.*, **9**, 501 (1930).
[3] *Ibid.*, **7**, 327 (1929).

" crystals " squeezes out excess water and mechanically occludes water globules in the kneaded mass. The most recent tendency is to emulsify the correct amount of water (16 per cent.) directly in the melted oil phase. An emulsifying agent such as Schou's oil serves well for this effect. Schroeder[1] carried out large-scale tests in this connection, using 0·5 per cent. of Schou's oil, and found that the W/O emulsion was stable up to 50° C., thus not requiring cooling during churning. The use of hydrogenated oils[2] has received investigation, as these apparently show considerable variation in their water-holding properties.[3] No satisfactory explanation is yet forthcoming.

Apart from technical procedure, including churning machines,[4] the patent literature on margarine deals largely with the addition of dispersing agents. The so-called " balanced emulsifying agents " (see p. 127) and Schou's P.E.O. (see p. 125) are notable in this connection. A German preparation, known as " Pancol," comprises a mono-diglyceride and a small proportion of sodium sulphoacetate.[5] The cetyl ester of sulphuric acid has been recommended.[6] Other additions claimed are lecithin,[7] soaps of hardened oils,[8] and aliphatic polyhydroxy substance incompletely esterified with a higher molecular weight polymerised or oxidised aliphatic acid such as the mono- and di-esters of glycerol formed by reaction of glycerol with polymerised soybean oil.[9]

SALAD DRESSINGS

Salad dressings may be either thin-flowing (salad cream) or viscous (mayonnaise). A salad cream may be made from a variety of ingredients, but mayonnaise is generally understood to be made from eggs, oil, vinegar and flavouring agents. Whilst no ruling has been given concerning the composition of salad creams, the Mayonnaise Products Manufacturers Association of America, Inc., recommended (January 24th, 1928) that[10]: "Mayonnaise, Mayonnaise Dressing, and Mayonnaise Salad Dressing is the clean, sound emulsified product composed of edible vegetable oil, egg-yolk or whole egg, a vinegar and/or lemon juice and/or other edible acids, with or without one or more of the following : salt, other condiments, sugar, edible stabilising material. In its preparation are used not less than 50 per cent. of vegetable oil and not less than 6 per cent. of fresh egg solids contained in commercial egg-yolk, dried egg-yolk or whole egg. In the finished product, the sum of the percentages of vegetable oil and fresh egg-yolk free from white is not less than 78 per cent. and the quantity of any stabilising material used does not exceed 2 per cent."

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[1] *Allgem. Oel. u. Fett-Ztg.*, **29**, 597 (1932).

[2] Pick, *ibid.*, **26**, 577 (1929); Schroeder, *ibid.*, **29**, 653 (1932).

[3] Bandau, *ibid.*, **30**, 10 (1933).

[4] For instance, continuous emulsification: McClean, U.S. 2,245,112 and 2,248,886 (1941).

[5] Erlandsen, *Fette und Seifen*, **46**, 147 (1939).

[6] Erlandsen, *loc. cit.*

[7] Noblee and Thörl G.m.b.H., Ger. 621,327 (1935).

[8] Harris, U.S. 2,024,355 (1935).

[9] Newton and Brown, U.S. 2,232,401 (1941).

[10] *Proc. Third Ann. Convention, Mayonn. Prod. Manfr. Assocn.* (1928), p. 18. Soybean protein as a stabiliser has been claimed by Gilmour, Can. 393,927 (1941). The lecithin/protein complex in egg yolk has been investigated by Sell, Olsen and Kremers, *Ind. Eng. Chem.*, **27**, 1222 (1935).

The latest official definition [1] is similar, except that "the finished product contains not less than 50 per cent. of edible vegetable oil." The published analyses of salad dressings and mayonnaises reveal wide variations in the amount of the various ingredients.

Salad creams and mayonnaise preparations are always of the O/W type, as would be expected from the fact that egg is used as the principal emulsifying agent. Until recently very little research had been made into the colloidal character of these emulsions, but increasing attention is being given to the use of egg-yolk and egg-albumin and to the type of machinery employed in emulsification. Much remains for investigation. No quantitative data is available regarding the emulsifying efficiencies of egg-yolk, egg-albumin and mustard.

According to Brooks [2] egg-yolk is preferable to whole egg as an emulsifying agent, since egg-white has only one-fourth the emulsifying capacity of the yolk. Robinson [3] found that frozen egg-yolk served to prepare stable emulsions, but they were unstable in transport. Dried egg-yolk is also a good emulsifying agent,[4] especially if initially dispersed in water at $pH = 8{\cdot}6$, *i.e.*, using alkali. A special egg-yolk preparation for salad creams contains glycerol and acetic acid.[5] Robinson reports that a mixture of powdered egg-albumin, milk albumin and gum arabic permitted very stable emulsions particularly adapted to withstand very low temperatures.

Mark,[6] adopting intermittent emulsification of 100 secs. beating and 10 secs. rest interval, found that "for 10 volumes of egg, 3 or less volumes of oil were always emulsified, while 4 or more volumes never were." Having now obtained this primary emulsion, he studied the volumes of oil which could be beaten in successively. They were 4, 7 and 12 volumes respectively. Working in this way it was immaterial whether a salad dressing was prepared with all ingredients at 55° C. or 0° C., and constant beating was as efficient as intermittent agitation when these volumes were adhered to.

Intermittent agitation is favoured by several of the investigators [7] (Smith, Whitacre and Mark). Regarding the speed of emulsification, preliminary results by Whitacre point to the relationship that "the time, or rather the total number of the revolutions is proportional to the cube of the volume of the oil added." All the data point to the advantages of beating-in a very slow and steady stream of oil rather than successive portions and best results are obtained when the oil is introduced beneath the surface of the aqueous phase, thus avoiding air/liquid interfering action (froth).[8]

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[1] U.S. Dept. Agric., Service and Regulatory Announcements (December, 1931).

[2] "Critical Studies in the Legal Chemistry of Foods" (New York, 1927), p. 145.

[3] *Am. Food J.*, **19**, 187 (1924).

[4] Cobb and Hunt, *J. Am. Leather Chem. Assocn.*, **21**, 18 (1926).

[5] Epstein, U.S. Pat. 1,595,765 (1926).

[6] Paper reprinted in Brooks' "Critical Studies in the Legal Chemistry of Foods" (New York, 1927), pp. 254 *seq.*

[7] See Brooks, *loc. cit.*, p. 258.

[8] Hall and Dawson, *Ind. Eng. Chem.*, **32**, 415 (1940).

The effect of diluting egg with vinegar was also investigated. Again the results are incomplete, but if 1 volume of egg is diluted with 8 volumes of vinegar, about 40 volumes of oil can be dispersed.

According to Bitting,[1] who prepared emulsions by shaking by hand and stored them for 90 days for examination of stability, the following are the ratios for stable emulsions :—

Cotton-seed Oil.	Vinegar.	Egg-yolk.
74	26	30
76	24	22·5
78	22	15
80	20	10
82	18	5
84	16	2·5

Kilgore [2] has emphasised that the nature, the origin and the method of addition of the mustard influence the emulsion to a marked extent. Corran [3] has also stressed the importance of mustard, and he has demonstrated its very efficient emulsifying capacity as a solid powder emulsifier. The effect was more noticeable when the mustard was incorporated with the egg-yolk at the onset. (Corran's paper should be referred to for a general investigation of the various factors concerned in the preparation of mayonnaise.)

On a commercial scale, whilst mayonnaise is made by careful mixing in a beater of the egg-whisk type, salad dressings are homogenised, usually in a two-stage homogeniser, a gum stabiliser being present in the mixture.

Gray [4] has published several papers dealing with mayonnaise as an emulsion. Discussing the " breaking " of mayonnaise, he refers to the two types of trouble familiar with marketed mayonnaise, viz. : (*a*) water separation below the emulsion, (*b*) oil separation above the emulsion. Gray outlines the various causes underlying these separations.

In the first place a correct quantitative relation between the ingredients is demanded, and this within only narrow limits. For instance, in a certain set of experiments with 78 per cent. of oil, 17 per cent. of water and 5 per cent. egg-yolk, a permanent emulsion was formed. If the amount of oil was reduced to, say, 76 per cent., the water increased to 19 per cent., the egg remaining the same, on standing the emulsion separated into two layers—a watery layer below and a creamy layer of emulsion above. If the percentage of oil was increased to 92 per cent., the egg remaining the same, the emulsion also separated on standing, but this time with an oil layer above and the emulsion layer below. If the amount of oil was decreased below 78 per cent. and the water increased, but the egg-yolk also increased, the emulsion formed was permanent. In general, the more water in an oil-in-water emulsion the more emulsifying agent is needed to make it permanent.

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[1] *The Canner*, **67** (xv), 32 (1928).

[2] *Glass Packer*, **11**, 621 (1932); **12**, 97 (1933).

[3] *Food Manfr.*, **9**, 17 (1933); " Technical Aspects of Emulsions " (London, 1935), p. 90.

[4] *Oil Fat Ind.*, **4**, 410 (1927); *Glass Packer*, **2**, 311 (1929).

The other causes of separation enumerated by Gray are: (1) adding the oil too rapidly, whereby dispersion is ineffective, and larger globules are coated with emulsifying agent; (2) not regulating the conditions of agitation, over-agitation leading to separation (cf. Herschel); (3) the effect of heat during storage; (4) the effect of freezing during storage; (5) agitation during transport; (6) bacterial spoilage.

The stability of salad dressings and mayonnaise has been studied by the aid of the Gardiner mobilometer.[1] The method is to note the time taken for a weighted plunger to fall through a given depth through the emulsion; this gives the consistency. Repeated readings on the same sample differ, the emulsion coarsening and ultimately even breaking as the number of times the plunger falls is increased. Gray and Soutnwick[2] reproduce excellent photomicrographs of such coarsening of the oil globules. This effect depends on the change which the protein emulsifying agent undergoes due to the formation of an air/emulsion interface, and parallels the present writer's method using a rotating wheel (see p. 433).

A defect in commercial salad dressings and mayonnaise is the development of rancidity on storage. Gray and Stone have described experiments in this connection, showing that rancidity may be inhibited by the incorporation of ascorbic acid and related compounds in the aqueous phase of the emulsion.[3]

PHARMACEUTICAL EMULSIONS

Administration of oils, often medicated, is facilitated by presenting the oil as an emulsion and many familiar emulsions are thus recommended. A very extensive literature has accumulated in this connection from which selection will follow.[4]

An olive oil emulsion containing liquid extract of male fern has been described by Elliot.[5] Moore[6] claims a medicament suitable for enteric assimilation containing oil of santal, whilst as an anthelmintic a tetrachloroethylene emulsion has been described,[7] and is referred to as "Tetram."[8] Other emulsions are benzyl benzoate stabilised by triethanolamine stearate for the treatment of scabies,[9] acriflavine emulsions,[10] ethyl aminobenzoate emulsions as topical anæsthetics,[11] nasal medicaments,[12] embalming composition,[13] suppositories,[14] colloidal sulphur emulsion,[1] and emulsions to act as detoxicants when used either subcutaneously or intravenously.[2]

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[1] See Kilgore, *Glass Packer*, **2**, 65; 90 (1929); Sward and Stewart, *Amer. Paint and Varnish Manfr. Assocn.*, Circ. **394**, 317 (1931); Baldeschwieler and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **11**, 525 1939); Combes, Ford and Schaer, *ibid.*, **12**, 285 (1940); Kinney, *ibid.*, **13**, 178 (1941).

[2] *Food Inds.*, **1**, 300 (1929); *Glass Packer*, **2**, 17; 77 (1929).

[3] *Food Inds.*, **11**, 626 (1939).

[4] See, for example, Kern, Büchner, Leopold and Momsen, *Apoth. Ztg.*, **50**, 691 (1935); Hall, *Pharm J.*, **135**, 133 (1935); Hazeloop and Puper, *Pharm. Weekblad.*, **65**, 217 (1928); Moncorps, *Arch. exptl. Path. Pharmakol.*, **141**, 25–104 (1929).

[5] *Pharm. J.*, **102**, 237 (1919).

[6] U.S. 2,066,572 (1937).

[7] Mönnig and Ortlepp, *Onderstepoort J. Vet. Sci. Animal Ind.*, **13**, 193 (1939).

[8] Mönnig, *Farming in S. Africa*, **13**, 146 (1938).

[9] Carslaw and Swenarton, *Brit. Med. J.*, **1941**, 226.

[10] Lum, *Pharm. J.*, **135**, 457 (1935); Trillwood, *ibid.*, **135**, 487 (1935).

[11] Beutner and Beutner, *Proc. Soc. Exptl. Biol. Med.*, **45**, 337 (1940).

[12] Painter, Cady and Henson, U.S. 2,013,524 (1935).

[13] Jones, U.S. 2,048,008 (1936).

[14] Chemisch-Pharmazeutische A.-G., Brit. 455,732 (1936); Ger. 667,500 (1938).

Carron oil (lime water + linseed oil in equal amounts) has long been known for the treatment of burns and has lately been reinvestigated.[3] In place of lime water, hypochlorite[4] may be employed to prepare a carron oil with excellent antiseptic properties. *Foille* has received strong recommendation for the treatment of thermal burns[5] and is a W/O emulsion containing about 97 per cent. of vegetable oil with anæsthetic and bacteriostatic ingredients and calcium ions.

For the treatment of constipation medicinal mineral oil is usually prescribed as emulsion, agar-agar being the chosen emulsifying agent,[6] Malt extract or a malto-dextrin syrup also serves.[7] The therapeutical claims made for the agar-agar present are unfounded, the amount being too small and the colloid being already fully hydrated.[8] The pharmacology of this long-established emulsion has been treated by several authors.[9]

Psyllium seed is now better known as an ingredient of paraffin emulsions,[10] whilst castor oil emulsions[11] or magnesium and calcium ricinoleate are also claimed.[12]

Cod-liver oil emulsions have had a long vogue.[13] The vitamin aspect of such emulsions is now stressed.[14] Bacterial spoilage has been discussed by Ruemele.[15]

AGRICULTURAL STRAYS

An extensive literature now pertains to the use of emulsions in agricultural sprays and only a summary of the main theoretical principles involved will be presented. Woodman's paper [1] should be consulted for a detailed exposition.

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[1] High, U.S. 2,138,546 (1939).

[2] Boericke and Young, Brit. 508,288 (1939).

[3] Clayton, Howard and Thomson, *Lancet*, **1941**, 341. See also Dann, Glücksmann and Tansley, *ibid.*, **1942**, 95.

[4] Tomb, *Med. Press*, **1928**, 99.

[5] Nagle, *J. Okla. State Med. Assocn.*, **33**, 14 (1940); Terrell, *Texas State J. Med.*, **34**, 409 (1938).

[6] *Am. J. Pharm.*, **90**, 203 (1918); McCutcheon, *Pharm. J.*, **110**, 365 (1923); Warren, *J. Am. Med. Assocn.*, **84**, 1682 (1925); Miller, U.S. 1,605,130 (1926), and Can. 277,180 (1928); Kelp-Ol Laboratories Inc., Brit. 317,713 (1928); Schulek and Vastagh, *Pharm. Zentralhalle*, **69**, 275 (1928); Knight, *Pharm. J.*, **121**, 297 (1928); Brown and Lum, *ibid.*, **131**, 341 (1933); Squibb, U.S. 1,913,561 (1933); Bateson and Long, *Pharm. J.*, **132**, 228 (1934); Lum, *ibid.*, **132**, 321 (1934); Griffith, U.S. 2,026,034 (1935); Machado and Sonol, *Rev. facultad cienc. quim.*, **12**, 47–78 (1937); Hulbert, U.S. 2,068,136 (1937).

[7] Hamburg, Brit. 26,390 (1913).

[8] Knight, *Pharm. J.*, **132**, 18 (1934).

[9] Schlagintweit, *Arch. exptl. Path. Pharm.*, **124**, 59 (1927); *Pharm. J.*, **119**, 461 (1927); Mellanby, *J. Physiol.*, **64**, (3), xxxiii (1927); Roth, *J. Pharmacol.*, **33**, 277 (1928).

[10] Noonan, U.S. 1,920,926 (1933).

[11] Bird, U.S. 2,021,044 (1935); Merrell and Bye, U.S. 1,862,315 (1932); Valentine, U.S. 1,804,135 (1931).

[12] Rider, U.S. 2,019,933 (1935).

[13] Buemming, *Apoth. Ztg.*, **29**, 695 (1914); Zölfl, *Pharm. Ztg.*, **59**, 542 (1914); Miyake *et al.*, Japan 35,730 (1920); Olsen & Co., Danish 36,481 (1926); Waggoner and Glover, *J. Am. Pharm. Assocn.*, **15**, 754 (1926); Obst, *Fortschritte Landw.*, **2**, 432 (1927); Jones and McLachlan, *Pharm. J.*, **121**, 91 (1928); *Quart. J. Pharm.*, **1**, 400 (1929); Rothenkirchen, *Pharm. Ztg.*, **79**, 804 (1934); Will, *Apoth. Ztg.*, **49**, 1443 (1934); Lepper, *Z. anal. Chem.*, **98**, 164 (1934); Deutsch Pentosin-Werke G.m.b.H., Ger. 593,395 (1934).

[14] Zernik, *Pharm. Ztg.*, **70**, 156 (1925); Griffiths, Hilditch and Rae, *Analyst*, **58**, 65 (1933); Valentin, *Pharm. Ztg.*, **76**, 1423 (1931); I. G. Farbenind. A.-G., Brit. 425, 988 (1933); Janes, Grover and Quinn, *Proc. Soc. Exptl. Biol. Med.*, **30**, xxx, 516 (1933); I. G. Farbenind. A.-G., Ger. 623,657 (1936); Rachevskii, *Z. Vitaminforsch.*, **6**, 203 (1937); Atlantic Coast Fisheries Co., Brit. 490,001 (1938); Briod and East, Brit. 506,730 (1939); Barton and Cox, U.S. 2,167,144 (1939); Brinton, U.S. 2,179,917 (1939).

[15] *Pharm. Zentralhalle*, **81**, 121 (1940).

The principal aim of agricultural sprays is the destruction of insects and their eggs on plants and animals, insecticidal and ovicidal sprays respectively. Fundamental in this connection as factors in the performance of contact insecticides are surface tension, surface activity and wetting ability. Toxicity alone is not sufficient; good spreading properties are demanded for the aqueous sprays.[2]

We have already noted (p. 216) that the equation for the equilibrium state when a drop of liquid rests on the surface of a solid is

$$\sigma_1 - \sigma_{1,2} = \sigma_2 \cos \theta.$$

where σ_1 = surface tension, solid/air,
$\sigma_{1,2}$ = ,, ,, solid/liquid,
σ_2 = ,, ,, liquid/air,
θ = angle of contact.

Complete wetting of the solid indicates zero angle of contact, the contrasting case of complete non-wetting would have a contact angle of 180°.

Many papers have examined the equation of wetting,[3] whilst the determination of contact angles has also engendered a growing literature.[4]

Martin [5] has been a prominent worker in this field and he has defined wetting and spreading properties: *Wetting* is the ability of the liquid to form a persistent liquid/solid interface when excess of liquid is drained from the surface. It is assessed by the receding contact angle and is perfect when this angle is zero. *Spreading* is the ability of the liquid to form a persistent liquid/solid interface solely by surface activity over the plain solid surface and is a function of the advancing contact angle.[6] Spreading must be distinguished from the penetration or creep of liquid through a porous solid, although the effect of a roughened surface is to magnify the wetting properties of the solid.[7]

Evans and Martin [8] in a laboratory evaluation of water-soluble wetting agents as constituents of combined washes, classifying these "spreaders" on a structural basis, examined such physical properties as spray retention, area of spread, contact angles and surface tension and found that the materials tested arranged in the same rough order of activity. Later, Fajans and Martin[1] discussed the physical properties of spray deposits affecting the efficiency of protective insecticides and fungicides. Their summary is quoted in part: The quantity of spray residue is determined by the initial amount deposited upon the sprayed surface (initial retention) and the ability of the deposit to withstand the action of the various agencies tending to its removal (tenacity). In addition, qualities of the spray deposit such as the uniformity of deposition (coverage) are concerned in relation to their effect upon the action of solubilising agencies (availability) and upon tenacity.

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[1] "Technical Aspects of Emulsions" (London, 1935), p. 57.

[2] O'Kane, New Hampshire Agr. Expt. Sta., *Tech. Bull.*, **39**, (1930); **40** (1930); **46** (1931); Wilcoxon and Hartzell, *Contr. Boyce Thomson Inst.*, **3**, 1 (1931). The *J. Econ. Entomol.* contains many papers in this field.

[3] Bangham and Razouk, *Trans. Faraday Soc.*, **33**, 1459 (1937); Ferguson, "Wetting and Detergency" (London, 1937), p. 11; Robinson, *ibid.*, p. 137; Sumner, *ibid.*, p. 15; Desalbres, *Bull. inst. pin*, **1936**, 79; Bartell, Alexander's "Colloid Chemistry," Vol. 3 (New York, 1931), p. 41.

[4] Mack, *J. Phys. Chem.*, **40**, 159 (1936); Mack and Lee, *ibid.*, **40**, 169 (1936); Lange and Nagel, *Kolloid-Z.*, **73**, 268 (1935); Sumner, "Wetting and Detergency" (London, 1937), p. 41; Adam and Shute, *ibid.*, p. 53; Ebeling, *Hilgardia*, **12**, 665 (1939); Wenzel, *Am. Dyestuff Reptr.*, **25**, 505 (1936); *Ind. Eng. Chem.*, **28**, 988 (1936); Kneen and Benton, *J. Phys. Chem.*, **41**, 1195 (1937).

[5] *Internatl. Congr. Entomol.*, **7**, 175 (1938).

[6] See the discussion between Sumner and Ablett, "Wetting and Detergency" (London, 1937), pp. 45–52. Spreading has been treated by Cupples, *Ind. Eng. Chem.*, **27**, 1219 (1935); **28**, 60; 434 (1936); Burdon, Fuller and Gibson, *Trans. Faraday Soc.*, **33**, 1528 (1937); Allen, Grant and Burdon, *ibid.*, **33**, 1531 (1937); Bangham and Saweris, *ibid.*, **34**, 554 (1938); Innes and Rowley, *J. Phys. Chem.*, **45**, 158 (1941).

[7] Wenzel, *Ind. Eng. Chem.*, **28**, 988 (1936).

[8] *J. Pomol. Hort. Sci.*, **13**, 261 (1935).

Later, the same authors dealt with factors affecting the retention and spray residue of emulsions and combined emulsion-suspensions.[2] They conclude that the initial retention of emulsions of sufficient stability for practical use is determined by the properties of the aqueous phase and is intermediate between that of the emulsifier solution alone and that of water. The extent of preferential retention of the oil phase increases as emulsifier concentration is reduced and is dependent on the character of the emulsifier. Thus, lime casein emulsions exhibit preferential oil retention to a greater extent than sulphite lye emulsions of equal stability, a phenomenon which does not appear to be related to the wetting properties of the aqueous phase. The initial and preferential retentions of emulsion-suspension systems are markedly affected by the extent of interaction between the emulsifier and the solid phase. This interaction, which though probably due to chemical reaction between the emulsifier and solid, is not always obvious from chemical data, results in partial or complete adsorption of the oil phase by the solid which is flocculated to large agglomerates.

If no such interaction occurs, the addition of solid has no effect on either the initial retention of the emulsion or free oil retention. If interaction occurs, the stability of the emulsion is reduced, with consequent increase in the extent of preferential retention of the oil phase. Preferential retention of the solid phase then becomes apparent.

The tenacity of the deposits from emulsion-suspension spray systems is favourably affected by the presence of oil but may be adversely affected by the emulsifier. With sulphite lye, for example, the adverse effect of the emulsifier outweighs the favourable effect of the oil, which is greater with cotton-seed oil than with highly-refined petroleum oil.

Owing to the necessity for using, in present spray machinery, sprays of high stability exhibiting but slow separation to layers of varying concentration, only emulsion-suspension systems showing little or no interaction between emulsifier and solid can be recommended for practical use. From this aspect sulphate lye appears to be the most suitable of the emulsifiers examined, and the disadvantage of its unfavourable effect on tenacity may be lessened by a reduction of emulsifier concentration.

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[1] *Ibid.*, **15**, 1 (1937).

[2] *Ibid.*, **16**, 14 (1938).

Since a balance must be made between the insecticidal efficiency of spray emulsion and its harmfulness to plants,[1] there must be careful regulation of the amount of the oil which will be deposited upon a surface.[2] The influence of the wetting and emulsifying powers of "spreaders" is thus important.

Ben-Amotz and Hoskins [3] point out that the application of a spray is a dynamic process during which there is rapid movement and surfaces and interfaces are constantly being changed. They therefore used high-speed photography to take pictures of emulsions as they were being sprayed upon a beeswax surface. The photographs were made after 10 seconds of spraying, the oil emulsions containing hæmoglobin and sodium oleate, respectively, to various concentrations.

The photographs in their paper reveal three distinct groups of wetting: (1) illustrated by the mechanical mixture without emulsifier and by the soap solutions, characterised by more or less hemispherical drops making a high angle of contact with the solid and rolling down the wax surface with little or no tendency to elongate or form long tails. The area of contact between the emulsion and the solid is relatively small and there is a correspondingly small opportunity for the oil globules to contact the solid surface. A low deposit would be anticipated. (2) A second type of wetting is exhibited by the hæmoglobin at 0·00093 per cent. and 0·00375 per cent. concentrations. The drops are much flatter, cover a larger area of solid surface and become much elongated as they roll down the surface. There is abundant opportunity for the oil globules to contact the solid, particularly as they tend to concentrate in the long tails behind the travelling globules of the emulsion. Deposit may be expected to increase as this condition becomes more marked. (3) The higher concentration of protein, 0·15 per cent., shows a third type of wetting, the elongated globules tending to merge into continuous streams and sheets which travel over the surface more slowly, so that a considerable portion of the solid is covered by them during most of the time the spray is being applied. Such continuous areas of liquid largely prevent the oncoming spray from gaining access to the solid and for this mechanical reason a decrease in deposit is to be anticipated.

As the authors point out such variations in the types of wetting shown by various emulsions as they are forcibly sprayed upon a solid are not indicated to the slightest extent by the ordinary methods of studying area of wetting or angle of contact under static conditions. They illustrate this thesis by photographs showing the behaviour while a mechanical mixture and emulsions were being sprayed and also the results when drops of these same sytems were placed on a wax surface when the initial changes in shape and area are almost complete within two minutes.

The mechanical and other factors affecting oil spray deposits have been listed by Hensill and Tihenko [4] who gave data under such headings as : deposit and globule size of oil on beeswax-coated surface with various periods of mixing of the emulsion ; pressure at pump and deposit ; time of exposure to spray and deposit ; distance from spray nozzle and deposit ; oil deposit on orange leaves and wax ; oil deposit in relation to drying time.

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[1] See, for example, Young and Morris, *J. Agr. Research*, **47**, 505 (1933); Young, *ibid.*, **49**, 559 (1934).

[2] See, for example, Tihenko and Hensill, *J. Econ. Entomol.*, **30**, 354 (1937).

[3] *Ibid.*, **30**, 879 (1937).

[4] *J. Econ. Entomol.*, **32**, 36 (1939).

Martin [1] has dealt with the evaluation of the wetting and spreading properties of spray fluids in a comprehensive paper. The importance of *p*H control is emphasised by Brown and Hoskins.[2] especially with sodium oleate or triethanolamine oleate.[3] The wetting characteristics of solids of low surface tension such as talc, waxes and resins have been discussed by Bartell and Zuidema.[4]

Recently Porter and Wyman [6] showed that hydrophobic multilayers deposited on a metallic plate gave contact potentials of about 70 mv. per layer. A most interesting account by Langmuir [7] followed, under the title : " Surface Electrification due to the Recession of Aqueous Solutions from Hydrophobic Surfaces." It is not surprising that this has led to a study of the *rôle* of electrical charges produced in spraying. Wampler and Hoskins [5] have shown that electrical charges are produced on globules by the rupture or atomisation of liquid columns and by the impact and splashing of globules against a surface. The rolling of globules and sliding of films over surfaces produce charges thereon. On sprayed beeswax surfaces charge varied greatly both in sign and magnitude, depending on the kind and amount of electrolyte present and the *p*H value of the spray. The charge-wetting relationship was investigated.

The physical chemist finds much of interest in the oil-mass theory of petroleum oil penetration into protoplasm, proposed by Young,[8] who investigated the effects of petroleum oil sprays and undiluted oils in the leaves and fruit of apple (*Pyrus malus L.*) and the penetration by oils and their subsequent distribution in plants. Oils were found in living cells ; hence his oil-mass theory. His conclusions from experimental work are : (1) oils entered apple leaves and were seen inside the vein and petiole-parenchyma cells and tracheæ. Sections of the attached stems showed oils inside the parenchyma cells of the cortex, medullary rays, and pith, and inside tracheæ ; (2) oils passed from potato leaves into the attached stems and tubers, and passed from turnip leaves into the attached petioles and tap-roots. Oils presumably enter living cells when they pass from living leaves into the tracheæ of attached stems.

" The oil-mass theory postulates that petroleum oil touches and mixes with oil-miscible substances concentrated in plasma membranes, forming a large mass with an oil continuous phase. Intercellular oil, oil between a cell wall and its protoplast; and the oily mass formed in cytoplasm are in contact, forming an oil-chain. Part of the oil flows and diffuses through, and flows with, this oil-chain into cytoplasm to various depths, aided by external forces such as those caused by gravitation, capillarity, and bending of tissues by wind."

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[1] *J. Pomol. Hort. Sci.*, **18**, 34 (1940).
[2] *J. Econ. Entomol.*, **32**, 57 (1939).
[3] Cupples, *J. Econ. Entomol.*, **31**, 68 (1938).
[4] *J. Am. Chem. Soc.*, **58**, 1449 (1936).
[5] *Ibid.*, **59**, 2476 (1937).
[6] *Ibid.*, **60**, 1190 (1938).
[7] *J. Econ. Entomol.*, **32**, 61 (1939).
[8] *Am. J. Botany*, **22**, 1 (1935).

EMULSION TREATMENT OF FRUIT AND VEGETABLES

Recently the advantage of coating fruit and vegetables with wax from emulsions has received renewed attention.[1] Patents have been granted in this connection.[2]

The most comprehensive account of the matter is that by Platenius [3] on the use of wax emulsions for vegetables. The idea underlying such treatment is the reduction in rate of water loss and wilting. So successful is the process that Platenius states that more than 75 per cent. of all the oranges grown in California and Florida are waxed.

The methods for making and applying the wax emulsions are outlined by Platenius whose investigations on the nature of the wax film led to the conclusion that the wax coating inhibits the diffusion of water vapour and other gases and that the rate of diffusion depends primarily on the solubility of the gases in the wax membrane.

The thickness of the wax film is proportional to the concentration at which the emulsion is applied, but the average thickness should be of the order of 1 to 2 microns. Continuity of film depends on suitable wetting and spreading. The commercial wax emulsions used contained paraffin wax (" Brogdex Wax," 3·4 per cent. paraffin wax + 0·6 per cent. mineral oil; " Dowax," 28 per cent. paraffin wax + 8·5 per cent. bentonite), sometimes with carnauba wax added, to total solids of 18 to 35 per cent. The surface tensions were mainly of the order of 32 to 37 dynes/cm.

The washed vegetables were, without drying, dipped into the wax emulsion of desired concentration at room temperature, and then drained up to 2 minutes. They were then air-dried on a wooden grate, an electric fan accelerating drying to about 10 minutes.

The results obtained with topped carrots and cucumbers were outstanding, and the application of wax emulsions to these crops is recommended without qualification. The waxing of leafy vegetables or bunched root crops always gave unfavourable results.

A physiological study of waxed and unwaxed carrots showed that the wax treatment caused a decrease in the oxygen consumption but had no noticeable effect on the CO_2 production. Because the respiratory quotient of stored carrots is normally less than one, the shift in the course of respiration is unlikely to have harmful effects. Chemical analyses indicated that waxing has a tendency to reduce sugar losses in stored carrots.

A related trend in this employment of emulsions concerns the preservation of eggs by coating with oils by means of emulsions of suitable composition.[4]

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[1] Van der Plank and Rattray, *Union S. Africa Dept. Agr., Rept. Low Temp. Research Lab.*, **1936/1937**, 151; Kaess, *Z. Ges. Kalte-Ind.*, **45**, 227 (1938); Fisher and Britton, *Sci. Agr.*, **21**, 70 (1940).

[2] Brogden and Trowbridge, U.S. 1,809,016 (1931); Harvey, U.S. 1,909,860 (1933); Bridgeman and Schade, U.S. 1,943,468 (1934); MacRill, U.S. 2,019,758 (1935).

[3] N.Y. (Cornell) Agr. Expt. Sta., *Bull.*, **723**, p. 43 (1939).

[4] Fowler and Benfield, Brit. 419,668 (1933); Chuck, U.S. 2,038,540 (1936); Schmidt, Brit. 496,659 (1938); Schmidt, U.S. 2,222,000 (1940).

TEXTILE EMULSIONS

The lubrication of textile fibres is usual in order to reduce friction between the fibres and between fibres and machine parts. Such oiling renders the material soft and pliable and is normally effected by the aid of emulsions. A wide literature has accumulated [1] and many patents have been granted. The physical chemistry of the matter embraces problems of adhesion, wetting and the subsequent removal (de-oiling) of the textile.

Speakman and Chamberlain,[2] dealing with emulsions and emulsification in the wool textile industry state that the amount of olive oil applied to wool in combing is 3 per cent. by weight, giving a film thickness of about 0·2 μ. Fundamental problems of boundary lubrication and adhesion are thus to be expected. The character of the fabric surface, the length of the molecule of oil used, and the polar nature of the oil are all important factors. The authors' very interesting experiments lead them to the conclusion that the ease of removal of an oil from wool depends on the distribution of oil-soluble polar compounds between the wool/oil and oil/water interfaces, on the magnitude of the oil/water interfacial tension and on adhesion.

The importance of the wetting power of the emulsion is reflected in the experiments of Neville and Marshall [3] on the soaking of raw silk in an oil emulsion. The newer wetting agents have been discussed by Speakman and Chamberlain,[4] who, however, point out that since the oil has served its purpose in processes prior to waving (wool) it has to be removed in piece scouring processes. As the emulsifying agent may serve a useful purpose in scouring, " the logical extension is to make the wool oil itself water-soluble, and a sulphonated oil of this type, Whitcol SFS, is now finding considerable use in the woollen industry."

In connection with the emulsion oiling of wool, Palmer and Blow [5] draw attention to the fact that oil deposits on wool if these possess opposing electrokinetic potentials. When such stabilisers as Lissapol, Igepon T or soap are used the oil is negatively charged and deposits on wool at a *p*H below 3·5, whereas with stabilisers like dodecyldimethylsulphomium methosulphate or cetylpyridinium bromide, the oil is positive and deposits at a *p*H greater than 7.

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[1] Mullin, *Textile Colorist*, **50**, 591 (1928); Herbig, " Die Oele und Fette in der Textilindustrie " (Stuttgart, 1929); Meunier and Corbière, *Compt. rend.*, **191**, 661 (1930); Corbière, " Sur la fixation des Matières grasses emulsionnees par les fibres textiles " (Lyon, 1931); Speakman and Franks, *J. Textile Inst.*, **23**, 154 T. (1932); Speakman and Chamberlain, *Trans. Faraday Soc.*, **29**, 338 (1933); Speakman, *J. Soc. Chem. Ind.*, **53**, 173 T. (1934); Speakman and Greenwova, *Textile Mfr.*, **61**, 281 (1935); Speakman, *Melliand Textilber.*, **16**, 538 (1935); Speakman and Greenwood, *J. Textile Inst.*, **26**, 271 P. (1935); Pingree, *Oil and Soap*, **12**, 182 (1935); Foulon, *Allgem. Oel-u. Fett-Ztg.*, **34**, 451 (1937); Wardrop, *J. Soc. Dyers Colourists*, **54**, 305 (1938); Schulz, *Fette u. Seifen*, **45**, 146 (1938); King, *J. Textile Inst.*, **30**, 379 (1939); Klenck, *Melliand Textilber.*, **20**, 737 (1939).

[2] Harvey's " Technical Aspects of Emulsions " (London, 1935), p. 101. See also Speakman and Wang, *J. Soc. Dyers Colourists*, **56**, 259 (1940). A related paper is by Schmidt, *Teintex*, **5**, 88 (1940). Townend, *J. Textile Inst.*, **31**, 31 T. (1940) deals with the amount of emulsion permissible.

[3] *Ind. Eng. Chem.*, **23**, 58 (1931).

[4] *Loc. cit.*, p. 109.

[5] *J. Textile Inst.*, **29**, 91 (1938).

CUTTING OILS

The employment of cutting fluids for machine tools is well established [1] and an ever increasing issue of patents demonstrates the interest given to this subject.[2]

The chosen fluid must possess anti-friction efficiency and the capacity to dissipate heat.[3] The action of a cutting tool has been described by Swift [4] with the planer tool as the prototype of all metal cutting tools except grinding wheels. He states that the perfect cutting fluid has still to be found. Its essential properties are a high specific heat, fluidity and good lubricating properties. It is, of course, necessary that it should also be non-corrosive, non-injurious, non-inflammable and stable.

According to Swift " the cutting fluids in common use fall into four groups : aqueous solutions, aqueous emulsions of soluble oils, straight oils (mineral, fatty or compounded) and ' doped ' oils (containing sulphur, graphite or other addition). Of these the solutions and weaker emulsions have specific heats about twice those of the oils and about 10 times those of the ordinary metals. Good fluidity also assists heat disposal by convection, and here again the aqueous groups are superior, water being a 100 times more fluid than an ordinary machine oil at ordinary workshop temperature. On the other hand, the surface tension of water greatly exceeds that of ordinary oils.

" The lubricating property of a liquid under the drastic pressure and surface conditions prevalent in metal cutting cannot be assessed by ordinary bearing standards. Viscosity, for instance, is no index of this property. It is essentially a surface as distinct from a mass property, and for that reason the ' active principle ' need not be in concentrated form. The efficacy of sulphur and graphite, for example, which has been demonstrated in a number of cases, is not materially improved by additions beyond a certain small proportion. Up to the present time no correlation has been established between the efficacy of a cutting lubricant and any other physical or chemical properties, and the only satisfactory method of assessment is by direct test with a cutting tool."

[1] Hartmann, *Chem. Weekblad.*, **20**, 59 (1923) ; Luttringer, *Mat. grasses*, **19**, 8040 (1927) ; **20**, 8068 (1928) ; Wingfield, *J. Inst. Production Engrs.*, **15**, 40 (1936) ; Halls, *Ind. Chem.*, **12**, 403 (1936) ; Beuerlein, *Aluminium*, **19**, 175 (1937) ; Aldridge, *Metal Working Press*, **2** (xi), 6 (1938) ; Huffman, *Metal Progress*, **33**, 584 (1938) ; Chilvers, *Petroleum Times*, **40**, 345 (1939) ; Lloyd and Beeny, *Can. Metals Met. Inds.*, **3**, 97 (1940) ; Robbe, *Mat. grasses*, **29**, 12 (1937).

[2] Sullivan, U.S. 1,773,123 (1930) ; Merrill, U.S. 1,739,686 (1930) ; Adams and Kittrell, U.S. 1,817,599 (1931) ; Gallsworthy, U.S. 1,874,956 (1932) ; Brown, U.S. 1,872,617 (1932) ; Lant, U.S. 1,861,398 (1932) ; Adams, U.S. 1,871,939 (1932) ; Wilkin, U.S. 1,907,920 (1933) ; Thorpe, Brit. 420,682 (1933) ; Rutherford, U.S. 1,944,273 (1934) ; Gallsworthy, U.S. 1,964,983 (1934), U.S. 1,987,397 (1935) ; Herrmann and Roehner, Brit. 468,685 (1935) ; Abrams, Brit. 428,463 (1935) ; Hendrey, U.S. 2,058,788 (1936) ; Herrmann and Roehner, U.S. 2,062,652 (1936) ; Neukom, U.S. 2,060,425 (1936) ; Hasenclever, Brit. 465,704 (1937) ; Cupit, U.S. 2,096,449 (1937) ; Holtzclaw and Winning, U.S. 2,079,803 (1937) ; Lincoln and Steiner, Can. 367,758 (1937) ; Continental Oil Co., Brit. 470,756 (1937) ; Brit. 471,593 (1937) ; Muskat, U.S. 2,112,677 (1938) ; Guthmann, U.S. 2,162,454 (1939) ; Kaufman, U.S. 2,167,439 (1939) ; Chittick, U.S. 2,181,964 (1939) ; Kobbe, U.S. 2,178,325 (1939) ; Dombrow, U.S. 2,124,634 (1940) ; Williams, U.S. 2,199,146 (1940) ; Pevere, U.S. 2,186,271 (1940) ; Steiner, U.S. 2,188,255 (1940) ; Corkery, U.S. 2,193,476 (1940).

[3] Heck and Bartlett, *J. Elisha Mitchell Sci. Soc.*, **52**, 166 (1936), deal with " Heat Transfer Across an Interface between Oil and Water."

[4] *J. Inst. Petroleum Tech.*, **24**, 662 (1938) ; *Engineering*, **146** (1938)

General reviews of this subject have been given by Philipp,[1] Miller,[2] Beard,[3] Mason,[4] and Lloyd and Beeny.[5]

CRUDE-OIL FIELD EMULSIONS

Crude oil emulsions—water emulsified in natural petroleum—constitute a major problem in oil recovery, as testify the numerous patents dealing with their de-emulsification. A very comprehensive and eminently practical survey entitled: " Oil-Field Emulsions " has been presented by Dow,[6] who also provides a good bibliography.

At least 20 per cent. of the oil produced in the Mid-Continent and Gulf Coast fields contains emulsified water.[7] Since the presence of " trapped water " increases production costs, such as lifting, its incidence is an important problem. Not only is the marketability of the oil affected, but corrosion of pipe-lines, pumps, etc., may occur. Again, the water must be removed before distillation of the oil in order to minimise losses due to frothing and to salt incrustations on the walls of the stills.

When water is present in the sand or gains access to the bore-hole, water-in-oil emulsions form,[8] the amount of emulsified water and its stability in dispersion varying geographically. Particularly difficult to resolve are *bottom settlings*,[9] the heavy emulsion which settles below in gravity sedimentation, accompanied by sand and silt and organic matter, such as wax thrown out by cold oil.

The method of raising petroleum to the surface affects the extent of emulsification; emulsions are common from wells which flow naturally under such gas pressure as to avoid the necessity of mechanical lifting. The initial quantity of water available is also important. Light contamination with water tends to emulsify all the water, whilst excess of water causes little dispersion with free water and oil and some bottom settlings. Indeed, water or brine[10] is sometimes run into the well deliberately, so as to increase the amount of available water that the formation of otherwise stable emulsions is avoided. This is an example of the familiar fact that addition of an excess of the internal phase to an emulsion tends to break it.

The water content ranges from traces to 90 per cent., the more common figure being about 25 per cent. The water globules vary from such fine dispersion as 1μ to coarse dispersions of $20—100\mu$.[11] Further, the water may be nearly free from solutes or may contain up to 25 per cent. of

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[1] *Allgem. Oel-u. Fett-Ztg.*, **33**, 545 (1936).

[2] *J. Inst. Petroleum Tech.*, **24**, 645 (1938).

[3] *Am. Machinist*, **83**, 111 (1939).

[4] *J. Inst. Petroleum Tech.*, **24**, 655 (1938).

[5] *Ibid.*, **24**, 650 (1938); *Can. Metals Met. Inds.*, **3**, 97 (1940).

[6] U.S. Bur. Mines, *Bull.*, **250**, 112 (1926). See also Garton, *ibid.*, *Repts. Investgns.*, No. 3130 (1931); Uren, *Natl. Petroleum News*, **21** (xiii), 51, 54, 56 (1929); Koetschau, *Z. angew. Chem.*, **32**, 45 (1919).

[7] Dow, U.S. Bur. Mines, *Repts. Investgns.*, No. 2,683 (1925).

[8] Occasionally O/W emulsions occur. See Ryazanov, *Chem. Abs.*, **24**, 1729 (1930).

[9] See McCoy, Shidel and Trager, *Mining and Met.*, **1919**, 3168.

[10] Mills, *Oils and Gas J.*, **27**, No. 49; 46, 150 (1929).

[11] Numerous photomicrographs are given by Dow, *loc. cit.*, 91 *seq.*, and by Abozeid, *Am. Inst. Mining Met. Eng.*, **Tech. Pub.**, **345**, 3—21 (1930).

NaCl.[1] Indeed, actual crystals of NaCl are sometimes seen in photomicrographs of crude-oil emulsions.[2]

The emulsifying agent serving to stabilise crude petroleum emulsions is probably asphalt, either alone or adsorbed on clay and other earthy matter.[3] We have already noted that clay itself can promote the emulsification of water in oil. Asphalt in its relation to the colloid chemistry of petroleum has been discussed by Dunstan,[4] Richardson,[5] Sherrick,[6] and Padgett.[7] It seems fairly agreed by most authorities that asphalt or other heavy hydrocarbons present in crude oils may be adsorbed on the earthy matter present, and this complex then forms a protective film about the water globules.[8] Frequently, petroleum in contact with water for several weeks causes the formation of a loose interfacial membrane which will support sand.[9] Apparently a high alcohol, C_nH_m.OH, which is present, is destroyed or inhibited if the water contains sodium carbonate.[10] That asphalt can act as an oil-soluble colloid promoting emulsification has been shown by Sherrick,[11] who prepared an emulsion of brine in pure white paraffin oil by the aid of 0·5 per cent. asphalt. Again, Richardson [12] has observed that the earthy matter in Trinidad asphalt possesses a high adsorption capacity for the bitumen in the asphalt. Finally, the presence of asphalt in petroleums has been confirmed by the ultrafiltration of petroleums, using vulcanised rubber membranes.[13] The resins of petroleum which are separable by 70 per cent. alcohol are not ultrafilterable.

According to Gurwitsch,[14] who worked with Baku petroleum oils, on passing from the lower fractions (S.G. 0·797) to the higher (S.G. 0·916), the surface tension increases, but the interfacial tension, oil/water, decreases. Thus, kerosene naphthenic acids (S.G. 0·961) with a surface tension of 31·8 dynes per cm. give an interfacial tension against water of only 1·88 dynes per cm. He states that asphaltic and resinous substances and naphthene soaps are responsible for the formation of emulsions, and actually emulsion films can be demonstrated.[15] A quantitative analysis of a solution of a resinous substance in benzene before and after shaking with water, proved the accumulation at the dineric interface. Shaking emulsions with Fuller's earth to adsorb asphaltic resin breaks the emulsions, as does the addition of $SnCl_4$ which precipitates the organic colloid materials.[1]

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[1] van der Minne, *World Petroleum Congr.* (**1933**).

[2] Cf. Francis, *Ind. Eng. Chem.*, **8**, 682 (1916).

[3] Cf. Dow, *loc. cit.*, 82 *seq.*

[4] *Brit. Assoc. Colloid Repts.*, **3**, 91 (1920); Alexander's "Colloid Chemistry," Vol. **3** (New York, 1931), 491.

[5] *Brit. Assoc. Colloid Repts.*, **3**, 98 (1920); *Chem. Met. Eng.*, 21 (Jan., 1917).

[6] *Ind. Eng. Chem.*, **12**, 138 (1920).

[7] *Chem. Met. Eng.*, **25**, 189 (1921). See also Marcusson, *Chem. Ztg.*, **51**, 190 (1927); Morrell and Egloff, Alexander's "Colloid Chemistry," Vol. 3 (New York, 1931), 503; Gurwitsch, *ibid.*, 523.

[8] Sherrick, *Ind. Eng. Chem.*, **13**, 1011 (1921).

[9] Nutting, *ibid.*, **17**, 1036 (1925).

[10] Cf. Kellermann and Bock, *Petroleum*, **28** (xx), 1 (1932).

[11] *Ind. Eng. Chem.*, **12**, 138 (1920).

[12] *J. Phys. Chem.*, **29**, 245 (1919).

[13] Zaharia and Lucatu, *Bul. soc. chim. România*, **12**, 90 (1930); cf. also Lottermoser and Calantar, *Kolloid-Z.*, **48**, 369 (1929).

[14] "Scientific Principles of Petroleum Technology" (London, 1926), p. 141.

[15] See the photomicrograph of a crude-oil emulsion after standing one year, Lottermoser and Calantar, *loc. cit.*, 363.

It has been proved by Sherrick,[2] in the case of Goose Creek (Texas) field oils, that the oil is the continuous phase, the water being dispersed in this as globules, carrying a negative charge. Sherrick used the electrical conductivity method to determine the type of emulsion, the technique being particularly suitable in this case for determining the phase relationships of the oil and water, as dissolved electrolytes, especially NaCl, were present even up to 10 per cent. concentration. If the aqueous solution were the external phase, the emulsion should readily conduct electric current. In Sherrick's tests, however, with electrodes 2 in. apart and a P.D. of 250 volts applied, no deflection was observed of the needle of a sensitive milliammeter placed in the circuit. A cataphoresis test confirmed that water was the internal phase, a conclusion substantiated by the work of Dodd [3] on Californian crude oils. According to Kuczynski [4] the sign of the charge on the water globules depends only on the reaction of the water ; if the reaction is acid, the charge is positive, and if alkaline, the charge is negative.

EMULSIONS AS FUEL

As fuel for internal-combustion engines emulsions of the W/O type have been claimed by several patentees. Thus, for use in a carburettor, water and hydrocarbon oils are emulsified with oleic acid soap.[5] Vance claims as a liquid fuel an intimate mixture of water and crude petroleum in the volume ratio 2 : 3, homogenised to a W/O system at a pressure of 7,000 lbs. per square inch.[6] A number of patents have been granted to Roberts [7] relating to a liquid fuel for burners or Diesel engines, from 4 to 10 per cent. of water being present in the oil, together with hydrophilic colloids such as casein or starch. Russell [8] describes a W/O emulsion of heavy hydrocarbon oil and water which is mixed with hot air (at 425° C.) blast prior to burning. Ashless coal-oil emulsions are mentioned in several patents. The coal, oil and water are ground together, the water receiving the ash. The ash-free coal is then ground with oil to a paste.[9]

Ditto deals with fuel oil emulsions in the operation of iron blast furnaces. The production of pig iron in a blast furnace involves the introduction of a W/O emulsion into the tuyere zone of the furnace, the oil in the emulsion being sufficient upon combustion to generate at least the amount of heat required to decompose the water vapour derived from the water to form CO and H in the presence of the C produced by the hydrocarbons of the fuel oil, whereby a gas of high calorific value and relatively low in total N is produced.[1] The idea has also been extended to the open-hearth furnace for steel.[2] A further patent deals with the set-up for introducing oil and water by proportioning pumps to a colloid mill, and injecting the resulting emulsion downwardly toward the stationary hearth and on to the upper surface of a pool of molten metal.[3]

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[1] Lottermoser and Calantar, *loc. cit.*, 376.
[2] *Ind. Eng. Chem.*, **12**, 133 (1920).
[3] *Chem. Met. Eng.*, **28**, 250 (1923).
[4] *Przemysl Chem.*, **11**, 188 ; 466 (1927).
[5] Explosions-Turbine-Studien Ges., Danish 21,974 (1917).
[6] U.S. 1,926,071 (1933).
[7] Brit. 434,109 (1935) ; 433,348 (1935) ; 434,180 (1935) ; 438,351 (1935) ; Fr. 773,810 (1934) ; 774,915 (1934).
[8] U.S. 2,033,010 (1936).
[9] Kiesskalt, Brit. 458,486 (1936) ; Ger. 676,045 (1939) ; 690,829 (1940) ; 690,831 (1940). See also Pawlikowski, Ger. 620,259 (1935).

FIRE FIGHTING

The patent literature contains numerous references to methods of extinguishing fires by the use of foams, often containing CO_2, with particular attention to the nature of the foam-stabilising agent.[4] Fires in tanks of benzene and other light oils are readily dealt with by foam.[5] In the same way fire may be prevented by covering the inflammable liquid with a " blanket " of a mixture of emulsion and CO_2 froth.[6]

However, it is not necessary to employ an emulsifying agent. Water properly sprayed will itself emulsify the inflammable oil and thus reduce quickly the hazard of fire. Well-known in this connection is the " Mulsifyre " system of Mather and Platt, Ltd., of Manchester,[7] which utilises the mechanical force of the applied water to produce a quick-breaking emulsion. Thus may fires of any inflammable liquid not miscible with water be extinguished in quite dramatic fashion. In the case of fuel oils, the emulsion formation is very obvious ; if the water sprayers are allowed to run for a minute or so, the emulsion extends to a depth of several inches below the surface and persists without any apparent change for a minute or so and about 5 hours are necessary for complete separation. In the case of the light spirits like benzene, the emulsion breaks so soon as the water is turned off, wherefore fires of such liquids can be extinguished only when the whole surface of the liquid is bombarded by the emulsifying spray. In the case of the heavier oils, the emulsion tends to flow over the surface, whereby the shielding from the spray of quite considerable areas does not interfere with flame extinguishment.

A special set of projectors or nozzles provides water thrown at a rate of 15 gallons per minute at not less than 40 lbs. per square inch. In the body of the nozzle is a scroll with an outwardly divergent hole drilled through it. The scroll imparts a rotary movement to the water and in the absence of a central hole, the discharge would take the form of a hollow cone. If the hole through the centre be parallel, the discharge would take the form of a hollow cone with a solid jet in the middle of it. The desired aim, however, is attained by the outwardly-divergent hole which causes a reduction in the velocity of the water through it and so the stream of water it delivers does not overpower the swirling component from the spray but when properly proportioned, the two blend and the discharge from the projector is remarkably uniform over the whole of the area covered.

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[1] U.S. 2,175,517 (1939).

[2] U.S. 2,157,181 (1939).

[3] U.S. 2,217,540 (1940).

[4] See, for example, Nagel, U.S. 2,148,275 (1939) ; Timpson, U.S. 2,188,066 ; 2,193,541; 2,196,042 (1940) ; Holman, *Fire*, **30**, 204 (1938) ; Cantacuzene, Fr. 842,146 (1939).

[5] Kattenstroth, *Feuerschutz*, **18**, 166 (1938) ; Schliemann, *ibid.*, **18**, 124 (1938).

[6] Fisher, U.S. 1,985,491 (1934).

[7] Kohsan, *Feuerschutz*, **16**, 148 (1936) ; Barclay, *Inst. Mech. Engrs.*, *Proc. Gen. Disc. on Lubrication* (Oct., 1937) ; Underwriters' Laboratories, Inc., Chicago : Report on " Mulsifyre " Projectors (August, 1937), pp. 77.

The method has application to attacking fires in ship's bilge, boiler fronts, open tanks of oil, electrical transformers, split fuel oil pipes, etc.

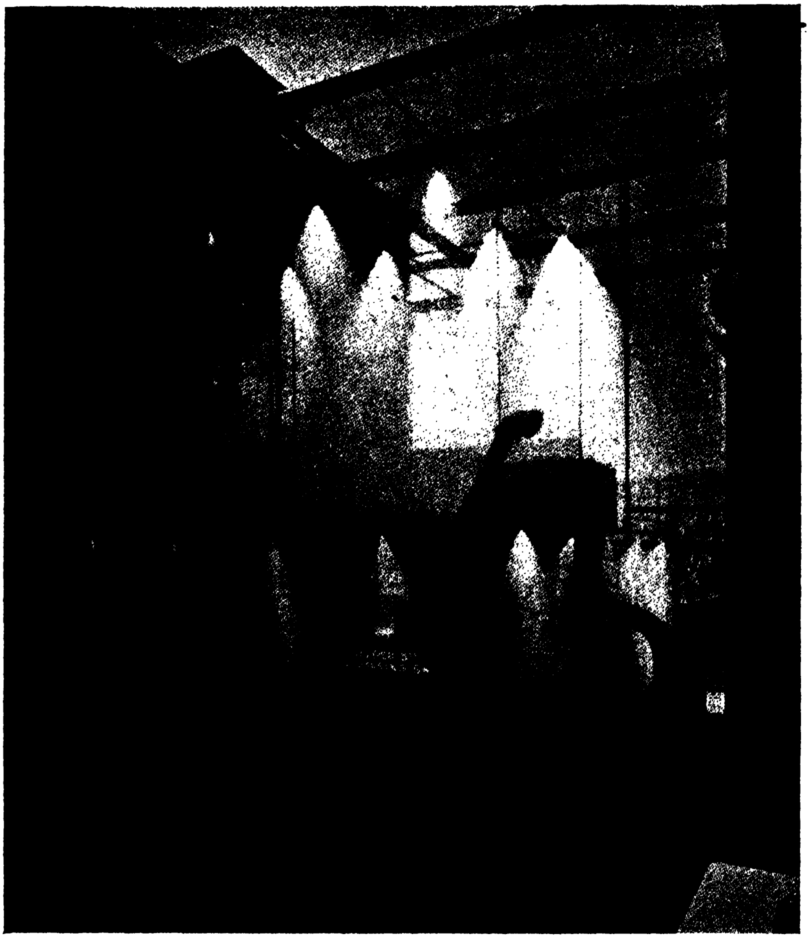

Fig. 49.

Its efficiency is seen in the fact that an oil fire can be extinguished by some 40 gallons of water discharged on the surface of a shallow tank, 2 feet deep, with a superficial area of about 600 square feet and containing 6,000 gallons of light fuel oil. Two to three seconds suffice to extinguish the conflagration from the moment of turning on the water sprays. (Fig. 49 illustrates an installation protecting a transformer station.)

CHAPTER X

THE PREPARATION OF EMULSIONS—BASIC PRINCIPLES

EMULSIFICATION is the art or practice of dispersing a given liquid as more or less permanent globules in another liquid medium. Stable emulsions of low oil content may be obtained by boiling a little oil in water for some time,[1] by dissolving oil in an organic liquid and then "precipitating" this solution in water, or by steam distillation (*e.g.*, of aniline). To make concentrated emulsions a suitable third substance must be added.

Emulsification is very important industrially, and numerous machines have been devised with a view to securing an intimate subdivision of the internal phase in the continuous medium. The chief principle involved is agitation of the two liquids either by means of revolving baffle plates or specially-designed stirrers, *e.g.*, screw propellers, worm screws, injectors, etc. The containing vessels are usually double-jacketed, so as to permit of temperature regulation by circulating steam or hot or cold water, as required. Usually emulsions are made in batches in tanks, but continuous-flow apparatus is now fairly common.

Besides agitation by mechanical means, other methods of mixing the phases are widely employed, and lately prominence has been given in the laboratory to electrical methods, particularly the use of ultrasonic vibration. The great variety of technical emulsions and especially the incidence of numerous emulsifying agents make the practical study of emulsification absorbingly interesting. In what follows it will be seen that empiric rules have long held sway, and in some cases the methods proposed are theoretically in fault.

Anyone familiar with the literature of emulsions cannot fail to be struck with the great variety of methods used by investigators to prepare emulsions. This fact, together with the lack of quantitative data on the size-frequency analysis of the emulsion produced, and the purely empirical manner of grading emulsion stability, make it impossible to use the great mass of information for the quantitative testing of any theory of emulsification. The present writer has made a plea [2] for the adoption of some standard method of preparing emulsions.

In general, the methods used to prepare emulsions in the laboratory are comparable with those on a technical scale, except that homogenisation of the laboratory primary emulsion is unusual. In view of the literature importance of Hatschek's transpiration method (adopted by several investigators) and Briggs' intermittent shaking method, and because of the remarkable reproducibility by a method due to Sumner, prior attention will be given to these purely laboratory operations.

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[1] Lewis, *Kolloid-Z.*, **4**, 211 (1909).

[2] *J. Soc. Chem. Ind.*, **45**, 288T. (1926).

HATSCHEK'S EMULSIFIER

Fig. 50 shows the simple apparatus required. The solution of emulsifying agent occupies about one-third of the cylinder. The oil to be emulsified flows very slowly from a pipette (P) through a funnel (F) and tube (T). Air is withdrawn from the cylinder by connecting outlet (B) to a pump. The slow flow of oil causes it to form a thin film on the inner wall of the tube (T) and the simultaneous out-passage of air at the bottom of the tube breaks up this film into finely-dispersed droplets. The air current also acts as a stirring medium for the system. Size-frequency analyses for emulsions prepared in this way have been given by Sibree,[1] who in one instance obtained dispersion of viscous paraffin in 1 per cent. aqueous sodium oleate, with nearly 90 per cent. of the oil globules with 20μ diameter.

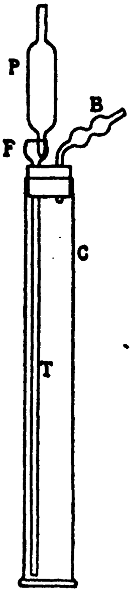

FIG. 50. Hatschek's transpiration apparatus.

SUMNER'S CONDENSATION METHOD

Instead of bringing about the disintegration of a bulk oil phase, Sumner [2] has utilised a condensation method from a vapour phase. This, of course, obviously limits its application to the preparation of emulsions having as the internal phase some organic liquid of boiling-point below that of water, the external phase.

Sumner injected the vapour of the disperse phase below the surface of the external phase which consisted of a solution of sodium oleate in water. Complications due to mechanical agitation (important in certain instances, as we shall see later) are absent.

The author points out that the range of diameters of the globules obtained by injecting a stream of " oil " vapour into the aqueous phase depends on (*a*) the conditions of injection, (*b*) the physico-chemical properties of the ingredients of the emulsion. Injection factors are the temperature and pressure of the vapour on entry, and the dimensions of the orifice of the jet. The vapour pressure and the jet dimensions control the velocity of the vapour. Important are the linear velocity imparted to the vapour molecules and the mass or volume of the vapour passing per second.

Fig. 51 illustrates the apparatus developed by Sumner, who describes it as follows : " Benzene is boiled by means of the heating coil A in the vessel B, which is provided with a trap bulb C. The vapour passes through the delivery tube D, jacketing the cylindrical bulb E, which is filled with nitrogen, to the bulb F. For clearness of drawing, the apparatus has been dissected in Fig. 51 ; in actual front view D is immediately behind F, the connecting tube (shown dotted) being about 8 cm. long so as to leave a clear space below the het. The vapour finally emerges *viâ* the trap G through the jet H. From C nearly to H, the tube is wound with nichrome wire on asbestos paper. All parts of the apparatus which are subjected to heat are lagged by winding with asbestos string. The temperature of the vapour is read on the thermometer J cemented into the bulb F, and the pressure on the manometer K, both values being measured as near as possible to the jet.

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[1] *Trans. Faraday Soc.*, **27**, 163 (1931).

[2] *J. Phys. Chem.*, **37**, 279 (1933); cf. Agthe, Brit. 210,307 (1923); U.S. 1,668,136 (1928). Sumner's method fails to give emulsions in the absence of emulsifying agents : Mészáros, *Z. Unters. Lebensm.*, **69**, 325 (1935).

"The bulb E forms a nitrogen thermo-regulator, and operates a mercury contact L controlling the relay M which in turn controls the current through the superheater coil. The temperature at which the regulator works is determined by adjustment of the nitrogen pressure by means of the mercury column N, the whole arrangement being essentially a constant volume gas thermometer. In this way the temperature of the issuing vapour may be maintained at any arbitrary constant value.

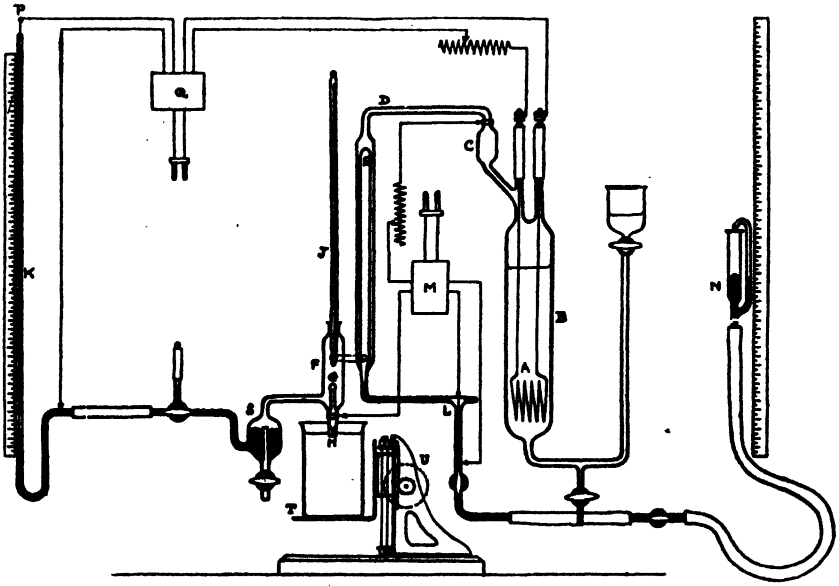

FIG. 51. Sumner's condensation apparatus for effecting emulsification under controlled conditions.

Automatic regulation of the pressure is provided by adjusting the contact P of the manometer to the desired value. This controls the current through the heating coil A by means of the relay Q. Since the rate of vapour formation governs the rate of efflux, equilibrium being reached at a pressure such that these two rates are equal, maintenance of a constant pressure is dependent on a steady rate of boiling, and this is achieved by the arrangement described. Power is taken from the mains (200 volts, D.C.), and a special relay circuit is used; except that whereas the relay Q brings extra resistance into the heating circuit when contact P is closed, as in the published arrangement,[1] relay M does so when contact L is opened.

"Taps are included in the apparatus at suitable points, for filling and draining the boiling vessel, for setting up and also for isolating the two manometric systems, and for draining distilled benzene from the bulb S. No tap is exposed directly to vapour.

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[1] *J. Sci. Instruments*, **7**, 398 (1930); *Trans. Faraday Soc.*, **28**, 20 (1932).

"A special device is used for introducing the beaker of dispersion medium quickly and accurately beneath the efflux jet. This comprises a stage T which is moved vertically by means of a rack and pinion U, and may be held in any desired position by a quick-release pawl (not shown). The beaker is placed on the stand, and the latter is quickly raised until the jet just dips into the liquid. After the required amount of vapour has been passed, the pawl is released, the stand quickly lowered, and the beaker withdrawn.

"The procedure in an experiment was as follows: The emulsification apparatus was started up and the oil vapour allowed to issue into pure water until a steady state was reached, under the desired conditions of temperature and pressure. A known volume of the dispersion medium, at a known temperature, was then quickly substituted for the water, and vapour was allowed to pass for the required time. The temperature of the emulsion having been noted, the beaker was then transferred to a special device in a water thermostat at 25° C., where the emulsion was kept stirred without free access of air."

Over the range of conditions investigated by Sumner the degree of dispersion of the benzene/sodium oleate emulsions was independent of the vapour temperature. Also, if the pressure of the vapour is not too low, the cross-section of the jet does not influence the grain-size of the emulsion. Increasing the pressure of the issuing vapour renders the emulsion more homogeneous, without considerable alteration of the mean size of the globules. For further details the full account given in the author's paper should be consulted.

BRIGGS' INTERMITTENT SHAKING METHOD

Interesting work on emulsification has been carried out by Briggs,[1] who, arguing that the *mode* of shaking a mixture of benzene and aqueous sodium oleate might be an important factor in emulsification, found that *intermittent* shaking was vastly more effective than the usual uninterrupted shaking. Briggs concluded that "intermittent shaking may be six hundred or even a thousand times more effective than uninterrupted but equally violent agitation."

Shaking by hand, mixtures of benzene in 1 per cent. aqueous sodium oleate, Briggs found that to emulsify 60 per cent. by volume of benzene 750 shakes were necessary, occupying 4·2 minutes without stopping. The same mixture could be completely emulsified with five shakes in less than one minute, if after two shakes a rest of thirty seconds was allowed. Similarly, to emulsify 80 per cent. by volume of benzene 6,300 shakes, occupying thirty-five minutes, were required when shaking continuously, but only forty-five shakes over a total period of four and a half minutes were necessary when thirty seconds' rest followed each two shakes.

The effect of varying the rest interval was also studied, emulsions being made of ninety volumes of benzene in ten volumes of 1 per cent. sodium oleate, shaking once up and down by hand.

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[1] *J. Phys. Chem.*, **24**, 120 (1920).

Rest Interval. Secs.	Total Shakes Required.	Total Time Elapsed. Minutes.
60	12	12
30	18	10
10	31	6
Nil.[1]	9,900	>60

[1] Uninterrupted shaking for over one hour.

From these results it is seen that the time required to form a complete emulsion with intermittent agitation passes through a minimum as the rest interval increases.

Robinson [1] reports that "there seems to be considerable agreement as to the advisability of introducing intermittent beating in the making of mayonnaise." He notes, too, that there is an optimum rate of addition of the oil. A fine stream of oil should be added at first, this being increased in volume as the batch increases in bulk and stiffness.

The explanation advanced by Briggs, to account for the very marked superiority of intermittent over continuous emulsification, is that efforts should be made to break up only the disperse phase of an emulsion, leaving the continuous phase as unbroken as possible; anything tending to disintegrate the continuous medium—sodium oleate solution in these experiments—will retard emulsification. Since globules of benzene in a soap medium are prevented from coalescing, it is obviously advantageous to keep the soap medium as continuous as possible. In uninterrupted shaking, some time must elapse before the soap solution is really disintegrated into drops, and hence the dispersion of benzene in the solution should be more rapid and effective during the initial stages of emulsification. This is found to be the case in actual practice.

The present writer believes that Briggs' explantion is only partially true. Shaking is an inferior method of making emulsions, because, as the emulsion becomes more perfect, the smashing action between the relatively heavy and light particles becomes more feeble, whereas the smashing forces should be increased. Accordingly, continuous shaking should give equally as good results as the intermittent shaking, provided the emulsified portions of the mixture are continuously removed from the mass, so that the energy of shaking is concentrated on the remainder. A centrifugal type of emulsifier might be developed to realise such emulsification.

If this view is correct, then where the dispersed phase is injected into the external phase, below the surface, intermittent injection would confer no advantage over continuous injection.[2]

Woodman [3] independently discovered the advantage of intermittent agitation in dispersing 5 c.c. benzene in 5 c.c. of 0.4 per cent. gelatin solution. His results when plotted (Fig. 52) give a smooth curve and entirely confirm Briggs' experiments. Woodman's explanation differs from that of Briggs or Clayton, and considers the phenomenon as due to adsorption. Whilst continuous shaking produces numerous globules and permits adsorption of gelatin at the numerous interfaces, this adsorption is repeatedly disturbed. On the other hand, intermittent agitation permits adsorption to be well established on the globules. The existence of a minimum time for emulsification by the intermittent method indicates that the rest period allowed between the shakes is that necessary for adsorption to be well established. This idea certainly warrants further investigation, and suggests a study of the degree of adsorption at the dineric interface in relation to time.

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[1] *Am. Food J.*, **19**, 186 (1924).

[2] Confirmation of this opinion has been reported by Hall and Dawson, *Ind. Eng. Chem.*, **32**, 420 (1940).

[3] *J. Pomol. Hort. Sci.*, **4**, 95 (1925).

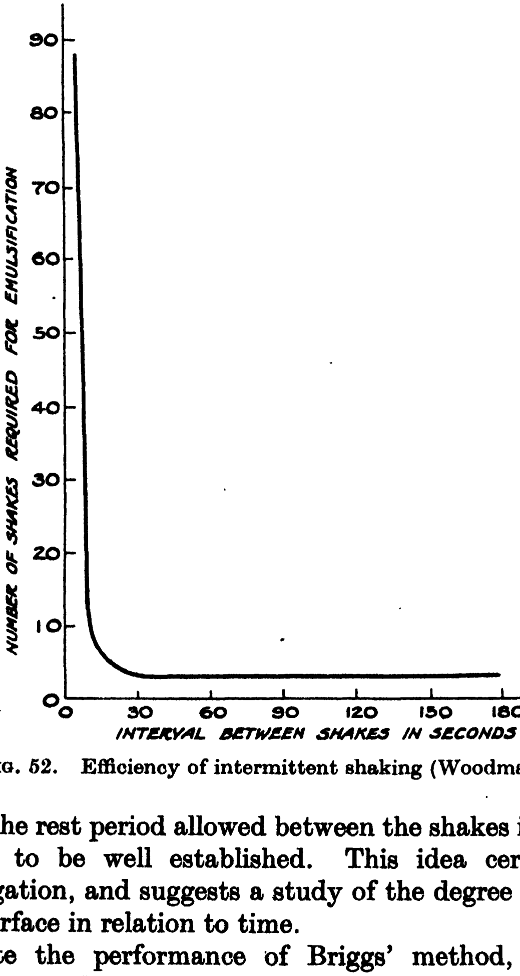

FIG. 52. Efficiency of intermittent shaking (Woodman).

To illustrate the performance of Briggs' method, the results by Sibree[1] may be cited. He emulsified paraffin in 1 per cent. aqueous sodium oleate, the oil being added in six equal portions to the soap solution; as each portion was added the mixture was shaken three times, a pause of about thirty seconds being made between successive shakings. With a viscous paraffin the size-frequency analysis of the emulsion was :—

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[1] *Trans. Faraday Soc.*, **26**, 26 (1930); **27**, 161 (1931).

Diameter of Globules.	Percentage Number of Globules.	Percentage Volume of Globules.
10μ	68·8	0·13
30	9·07	0·47
50	4·34	1·03
70	7·49	4·92
90	4·34	6·06
110	0·98	2·50
130	1·57	6·61
150	0·98	6·35
170	0·39	3·70
190	—	—
210	0·79	13·94
230	—	—
250	0·2	5·88
270	0·2	7·40
290	0·59	27·50
310	—	—
330	0·2	13·50

FACTORS IN THE PREPARATION OF EMULSIONS

In the following chapter attention will be devoted to the various types of apparatus employed in the technical preparation of emulsions. Certain observations relating to the different factors concerned must necessarily precede such discussion in order properly to appraise the technical methods. What we may term the mechanics of emulsification are far from being understood even now, although numerous emulsions of the most diverse constituents are made in every-day industrial operations.

INFLUENCE OF TEMPERATURE

The effect of rise in temperature is, in general, to make emulsification easier. Reduction of viscosity is obviously a factor concerned. The main interest, however, lies in the relation of temperature to the interfacial tension and the adsorption of the emulsifier at the interface. For non-miscible liquids rise in temperature is accompanied by a decrease in the interfacial tension, a condition favourable to emulsification.[1] In the case of partially-miscible liquids, the interfacial tension as a rule diminishes with rise in temperature, but instances are recorded where the interfacial tension increases, *e.g.*, at the interfaces : carbon disulphide/water, ether/water, triethylamine/water, octyl alcohol/water.[2]

Experiments on the connection between temperature and ease of emulsification have been carried out by Woodman.[3] Employing Briggs' intermittent shaking method, with the number of shakes required as the index, he found that the dispersion of 20 c.c. of toluene in 10 c.c. of 0·4 per cent. sodium oleate solution over the range 20° to 60° C. was greatly facilitated by rise in temperature. With 0·3 per cent. of gelatin as emulsifier, temperature change did not have any marked effect. In this case, however, viscosity (increased by ageing of the gelatin solution) had a pronounced effect at constant temperature (15° C.), emulsification becoming increasingly difficult as the viscosity of the continuous phase increased.

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[1] See Heymann, *Kolloid-Z.*, **52**, 275 (1930).

[2] Cf. Freundlich, " Colloid and Capillary Chemistry " (1926), p. 95 ; Rideal, " Surface Chemistry," p. 99 ; Du Noüy, " Surface Equilibria of Biological and Organic Colloids," p. 171.

[3] *J. Pomol. Hort. Sci.*, **4**, 100 (1925) ; *J. Agric. Science*, **17**, 55 (1927).

In certain technical instances, advantage may be taken of the viscosity factor. Thus, although a margarine emulsion is easily made by "churning" milk and oils at 50° to 60° C., cooling this emulsion with constant agitation, to about 28° to 30° C., yields a custard-like creamy emulsion of great stability. The thickening is due to the near approach to the solidification point, and the stable dispersion condition persists after the instantaneous chilling by a spray of ice-water or by feeding on to a brine-cooled rotating drum.

Similarly, in the preparation of mayonnaise, Gray and Maier [1] recommend emulsification at the optimum consistency, attained at about 18° C.

The change of solubility of the emulsifying agent with temperature may complicate matters. Thus, in the use of stearin or wax to promote water-in-oil emulsions, the agent is first melted in the hot, fatty phase. On cooling to a suitable temperature, the agent now becomes distributed throughout the fatty phase in solid form. A problem for investigation would be the effect of the *rate* of cooling, as the grain-size of the stearin or wax may play a *rôle*.

INFLUENCE OF DEGREE OF AGITATION

The prevalent idea regarding emulsification is that the oil and aqueous phases should be agitated together as violently as possible. so that small globules might result, thus tending towards a more stable emulsion. Consequently an empirical limit only is set on emulsification practice,[2] which is greatly in need of thorough investigation on the effects of different methods of agitation, and the degree of any one kind, on mixtures of oils and aqueous phases. It is well known that one can both make and break an emulsion by agitation. Thus Sheppard,[3] working on the emulsification of nitro-benzene in sulphuric acid, found that "de-emulsification was accelerated by slow shaking, or even single vibration in some cases, for emulsions which remained stable at rest, while shaking gently at slightly higher frequency would re-emulsify, to a system again stable at rest." Ayres [4] found that agitation (within reasonable limits) tends rather to increase than to diminish the size of globules of oils emulsified in aqueous soap solutions. The effect is somewhat comparable to the formation of butter from cream by churning, *i.e.*, by prolonged agitation.

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[1] *Glass Packer*, **4**, 23, 40 (1931).

[2] *Vide* Clayton, "Theory of Emulsions and Margarine Churning," *Margarine J.*, 2 (13), 503 (1920).

[3] *J. Phys. Chem.*, **23**, 634 (1919).

[4] *Chem. Met. Eng.*, **22**, 1059 (1920).

As Scoville [1] pointed out, " oil may be separated from a good emulsion by over-manipulation."

Another instance of a limiting degree of agitation in emulsification is given by Nugent,[2] who found that gentle agitation favoured the formation of emulsions of benzene in aqueous gelatin ; vigorous shaking (under the conditions of his tests) caused de-emulsification.

Woodman [3] dealing with the systems cresylic acid-gelatin-water, found that, in certain instances, the type of emulsion depended primarily on the mode of preparation. Using Briggs' method, gentle, short shakes or previous partial rotation of the container favoured the oil-in-water type ; vigorous, long shakes favoured the reverse type. Similarly, Seifriz [4] found that an emulsion allowed to stand and then re-shaken might reverse its type. Some quite inexplicable results were obtained, leading this author to write : " It is such idiosyncrasies of emulsions which try the patience of the investigator."

Harkins and Beeman,[5] investigating emulsions of petroleum oils in soap solutions, found that the method of mixing had an effect on the globule-size of the emulsion. A high-speed drink mixer gave a finer dispersion than did a motor-driven egg-beater, whilst " in general, the number of large drops decreases with the time of stirring, readily at first, and more slowly later."

It is quite reasonable to believe that for any given emulsifying apparatus there exists an optimum speed or degree of agitation or mixing, and an optimum time of running, whereby the most perfect emulsion can be attained for a given system.[6] Experiments prove this to be correct. Bechold, Dede and Reiner [7] found that the formation of emulsions of water and organic liquids plus finely-divided solids reaches an optimum after ten minutes' standard shaking.

Stamm,[8] by means of size-frequency analyses of emulsions of benzene in soap solutions, observed that the method of preparation affects the degree of dispersion of benzene-in-water emulsions to a marked extent, thus confirming the results of Harkins and Beeman, as reflected in their size-distribution curves.

Herschel,[9] in his studies on the resistance of lubricating oils to emulsification in water, has investigated the effect of duration of stirring and of speed agitation. He adopted five minutes as the time for agitation (using an electrically-driven paddle) in all his tests, having found that no marked increase in stability of the resultant emulsions followed longer agitation. In regard to the speed of stirring his mixtures of five different oils and water, he found that, in general, there is a speed above which the stability of the emulsions decreased, *i.e.*, the curve representing the relation between speed and stability passes through a minimum. Fig. 53 is reproduced from Herschel's paper; the abscissæ represent speed in hundreds of revolutions per minute, whilst the ordinates measure stability in terms of the number of cubic centimetres of clear oil rising to the top of the emulsion per hour. He adopted a speed of 1,500 r.p.m. as giving, on the average, a minimum rate of settling.

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[1] Scoville, " The Art of Compounding " (1895), p. 82.

[2] *Trans. Faraday Soc.*, **17**, 703 (1922).

[3] *J. Phys. Chem.*, **30**, 672 (1926).

[4] *J. Phys. Chem.*, **29**, 839 (1925).

[5] *Proc. Nat. Acad. Sci.*, **11**, 635 (1925) ; *J. Am. Chem. Soc.*, **51**, 1688 (1929).

[6] *Vide* Newman, *J. Phys. Chem.*, **18**, 38 (1914) ; also Pollard, *Pharm. J.*, **83**, 135 (1909).

[7] *Kolloid-Z.*, **28**, 7 (1921).

[8] *Colloid Symposium Monograph*, **3**, 251—267 (1925).

[9] U.S. Bureau of Standards, *Technological Papers*, No. **86**, pp. 1—37 (1917). See also Yates and Watson, *J. Soc. Chem. Ind.*, **59**, 63 T. (1940).

A comprehensive investigation has been reported by Mohr and Eichstädt[1] in connection with the churning stage in the making of margarine. The importance of the degree of agitation was quantitatively observed.

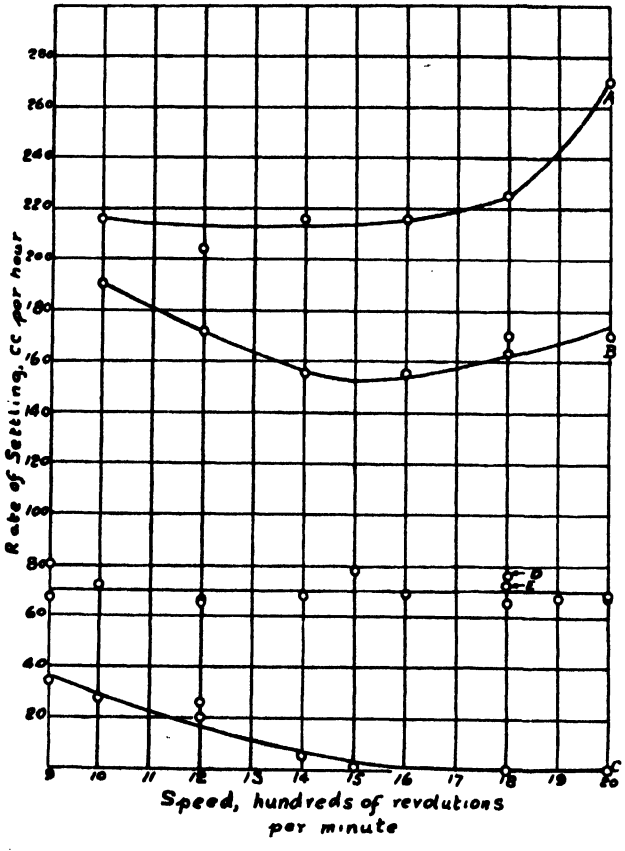

FIG. 53. Effect of speed of paddle upon rate of settling (Herschel).

A small laboratory test churn of 3,000 c.c. capacity was employed, fitted with two wings or blades (diameter = 12 cm.) revolving in opposite directions. Since " the result of an emulsification process depends on the power with which the emulsion substances are mixed," the optimum blade speed was sought. " The minimum number of revolutions (or peripheral velocity) below which stable emulsification is not practicable is in the present instance 667, this being true, of course, for our test churn only; for other churns, the critical number of revolutions will differ."

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[1] *Margarine-Industrie* (1932), Nr. 16/17.

Again, the authors point out: “In practice the opinion is often held that the peripheral velocity of the wings of the churn alone suffice to determine emulsification and that this figure could hold for all types of churns. However, this opinion overlooks that the kind of vanes and their relative disposition, as well as their respective direction of rotation, are factors which also have a pronounced influence on mixing and emulsification.”

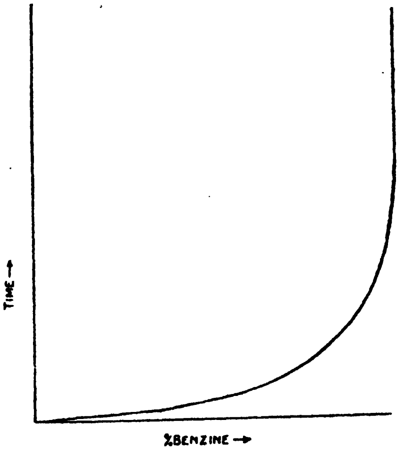

FIG. 54. Emulsification in relation to time (Briggs and Schmidt).

Briggs and Schmidt[1] have studied various factors influencing the emulsification of benzene in 1 per cent. sodium oleate solution, and found that the results depended on the size and shape of the containers and the speed and mode of agitation. Some interesting determinations were made of the time required to emulsify completely mixtures, containing different relative amounts of benzene and soap solution, at room temperature, keeping the combined volumes of benzene and soap solution constant at 50 c.c. The emulsions (oil-in-water type) were made in 125 c.c. bottles placed in a shaking machine, giving a lateral motion of approximately 400 oscillations per minute. It was found that the amount of shaking required increases, at first slowly with increasing volumes of benzene, and then rapidly, until the amount of shaking required becomes infinitely great.[2] Fig. 54 is the graph obtained by plotting the following results, the abscissæ representing per cent. by volume of benzene, and the ordinates the time in minutes required for complete emulsification.

Per cent. Benzene (by Volume).	Time (in minutes) for Complete Emulsification.
99	Incomplete after eight hours.
96	125
95	40
90	23 (22)
80	17 (11)
70	10
60	7
50	3
40	2
30	<1

From the graph the practical significance of such results is obvious, inasmuch as an excessive expenditure of power in making an emulsion is unnecessary, an optimum working time being readily ascertained.

These results would, of course, be altogether different if the increasing volumes of benzene had been added *gradually* instead of in bulk. Indeed, the most reliable method of obtaining stable concentrated emulsions is to add the disperse phase gradually, agitating at the same time.[1]

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[1] *J. Phys. Chem.*, **19**, 478 (1915).

[2] Cf. *J. Phys. Chem.*, **24**, 120 (1920).

Moore[2] has investigated the effect of the time of mixing on the size of aqueous globules dispersed in kerosene, using lamp-black as the emulsifying agent. He found that the size of the water droplets for any given mixture of ammonium chloride solution, kerosene and lamp-black passes through a minimum when the time of stirring is varied.

The complexity of the problem of emulsification has been discussed by the present writer[3] in a paper on "The Theory of Emulsions and Margarine Churning." After pointing out that in "churning" oils with milk, an oil-in-water type of emulsion is predicted, owing to the presence of the milk-colloids, it was stated: "Even when using milk and oils, *i.e.*, when the purely *physico-chemical* conditions are satisfied, different *mechanical* treatment may lead to an emulsion of the water-in-oil type. On consideration of volume factors alone (oil, 84 parts + aqueous phase, 16 parts), it will be evident that if one has the oil phase in bulk and then slowly runs in the milk phase, stirring continually, the conditions from the purely mechanical aspect of disintegration of particles favour the formation of an emulsion of milk in oil." Again, it was stated that if a stable emulsion of oil in milk, prepared by running the oil slowly into the milk phase with uninterrupted stirring, be passed through a high-speed continuous flow emulsifier, actual inversion of the emulsion will sometimes occur.

The relation of the quantity of liquids used to the cubic capacity of the mixing vessel plays a part in emulsification. This was investigated by Mohr and Eichstädt in their work on margarine churning, who found that whilst up to medium filling of their churn gave good emulsions, overfilling resulted in poor emulsification. "This fact can only be explained by reason of the relations of the various currents in the churn and the vortex conditions being changed."

AGITATOR PERFORMANCE

There exists a great variety of agitators intended for mixing solids or liquids with liquids. Many of these are described by MacLean and Lyons.[4] Propeller-type mixers have been studied by Bissell[5] who pithily states the problem thus: True mixing requires that dispersion of the different materials end with uniform relationship throughout the mix, whether large or small samples are involved. This can be accomplished only by setting up currents within the tank in such a way that differentials in direction and velocity occur in a multiplicity of loci. It is along the margins of these streams that actual mixing takes place, as well as directly at the propeller. One fact has been well proved : The existence of swirl or vortex indicates poor mixing since there is no interchange of position between particles under such conditions. The off-centre principle of agitation does away entirely with swirl or vortex and thus secures uniformity in a shorter time than other methods. Since no baffles are required, power requirements are usually lower.

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[1] Cf. Blichfeldt, Brit. 8,227 (1912). Thus, Auerbach injects the disperse phase into the circulating continuous medium; *Kolloid-Z.*, **74**, 285 (1936).

[2] *J. Am. Chem. Soc.*, **41**, 944 (1919).

[3] *Margarine J.*, **2** (xiii), 503 (1920).

[4] *Ind. Eng. Chem.*, **30**, 489 (1938). See also Gunness and Baker, *ibid.*, **30**, 497 (1938), and the well-illustrated summary in *Food Inds.*, **9**, 109 (1937).

[5] *Ind. Eng. Chem.*, **30**, 493 (1938). Data for the design of simple paddle agitators are given by White and Summerford, *Chem. and Met. Eng.*, **43**, 370 (1936).

Although a number of reports have dealt with such matters as power measurements in agitation,[1] the use of ultra-slow-motion photography to study drop formation,[2] power consumed by rotating discs in fluid media,[3] and the friction of a rotating disc against a liquid,[4] much remains to be elucidated in the actual production of emulsions as distinct from single liquids or even two immiscible liquids free from added emulsifying agents. Thus, Hixson and Luedeke [5] have investigated wall friction in liquid agitation systems, especially the relation between power input and stirrer speed, vessel diameter, liquid depth, stirrer pitch and fluid properties. However, the results obtained with a sugar syrup cannot be correlated with liquid/liquid systems, but are only indicative of the technique to be employed in laboratory work.

Yates and Watson [6] have made preliminary measurements of agitator performance by determining the rate of transfer of an indicating substance (water-soluble methyl red) from one liquid (0·2 per cent. aqueous acetic acid) to another immiscible liquid (kerosine). The transfer coefficient in conjunction with the power required by the stirrer gives the efficiency.

It was found that within a certain range the logarithm of the transfer coefficient for the dye bears a linear relation to the rate of stirring, while there is also a linear relation between the logarithm of the power and the logarithm of the rate of stirring.

TIME OF MIXING

Dodd [7] has described an optical method for determining the " time of mixing " of two transparent, not too readily miscible liquids. The method is an adaptation of the method of striæ, Toepler's *Schlierenmethode*, the aberrational effect on the rays of light passing through a medium exhibiting physical inhomogeneities. Variations in optical density cause refractive index changes from point to point, detectable by the scattering effect upon a beam of light transmitted through the medium. Mixing being completed, the striæ vanish, as noted by the clearing up of a real image formed by the traversing rays.

The " time of mixing " is the elapsed time required under the experimental conditions for image to clear up. It depends on such factors as the liquids to be mixed and the " rate of stir," which varies as the design of the stirrer, its size, shape, and amplitude of motion relative to the shape and size of the vessel and the total volume of liquid therein, the location of the stirrer in the vessel and the nature and rate of its motion. A temperature effect may be superimposed.

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[1] White, Brenner, Phillips and Morrison, *Am. Inst. Chem. Eng.*, May 14—16, 1934.

[2] Esselen and Hildebrand, *Trans. Am. Inst. Chem. Eng.*, **32**, 557 (1936).

[3] Fahrenwald and Staley, U.S. Bur. Mines, *Rept. of Investigations*, **3006** (1930).

[4] Kanaev and Hel'man, *Chem. Abs.*, **34**, 4306 (1940).

[5] *Ind. Eng. Chem.*, **29**, 927 (1937).

[6] *J. Soc. Chem. Ind.*, **59**, 63 T. (1940).

[7] *J. Phys. Chem.*, **31**, 1761 (1927).

Dodd used a metal meshwork stirrer with a nearly simple harmonic vertical motion in and out of the liquid. The liquid/liquid systems were: gasoline/carbon disulphide and water/saturated aqueous sodium chloride.

"The mixing process in general must consist in the production of striæ that are made finer and finer until they finally 'disappear.' This disappearance may be nothing more than the breaking up of the fine striæ, regarded as true films, into microscopic or ultra-microscopic droplets, in the same way a soap bubble bursts into fine droplets of soap water. . . . The question arises whether two stages of the mixing are to be recognised: (1) the mechanical dividing up of the two constituent liquids into striæ sufficiently small so that as very thin films they will start to break up into minute droplets; and (2) the breaking up of the striæ in this manner. It may be supposed that the breaking up in itself requires time, after the striæ have been reduced sufficiently in size—with some action of a physico-chemical nature. These two supposed stages of the mixing process may conveniently be termed the *primary mixing* and the *secondary mixing* respectively. The total mixing time as measured in the present experiments would then include both times of mixing, proceeding simultaneously and overlapping."

Dodd's very extensive report should be consulted for the experimental data presented although not directly dealing with three-phase systems. Interesting possibilities for further research were shown in the cases: gasoline ——→ carbon disulphide and carbon disulphide ——→ gasoline, over the range 3·3 to 95 per cent. gasoline. Plotting the time of mixing as ordinates and per cent. gasoline as abscissæ, the graphs coincide (as a straight line) up to 50 per cent. abscissæ value. Erratic values and changes in the character of the graphs occurred thereafter with a maximum time of mixing of 300 to 350 secs. at about 65 per cent. Apparently, the striæ of carbon disulphide in gasoline are longer lived than striæ of gasoline in carbon disulphide.

A detailed study of the mechanical factors involved in the tank-mixture method of preparing insecticidal oil sprays has been reported by Smith.[1] In principle he defines the tank-mixture spray as one wherein the water, emulsifier or spreader, and the oil are separately added to the spray tank, emulsification being produced and maintained by the agitators. "The efficiency of agitation depends on the capacity, shape, and dimensions of the spray tank; the number and position of the agitators; the size, shape, pitch, and number of blades on the agitators; the position of the agitator shaft; and the speed at which it turns. The efficiency is sometimes affected to a marked extent by braces, supports, and cooling pipes which operators occasionally place in their tanks. The uniformity of the spray mixture is also influenced by the character of the emulsions used and by the manner in which they are placed in the tank." This undoubtedly summarises the experience of all technologists who have had to engage in large-scale production of emulsions.

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[1] Univ. Calif., Agr. Expt. Sta, *Bull.*, **527** (1932), pp. 84.

Two types of common tanks are widely used; the half-round bottom and the elliptical bottom; in the latter the bottom may be uniformly rounded or the bottom may be almost flat along the middle portion with sharp shoulders at the sides.

Fig. 55 from Smith's report illustrates types of agitators normally used in southern California for making oil sprays. Two-bladed and three-bladed agitators form the two types. Table 45 by Smith relates to these agitators and he states that forms B, E and H are unsatisfactory, whilst forms A, C, D and G are specially suitable.

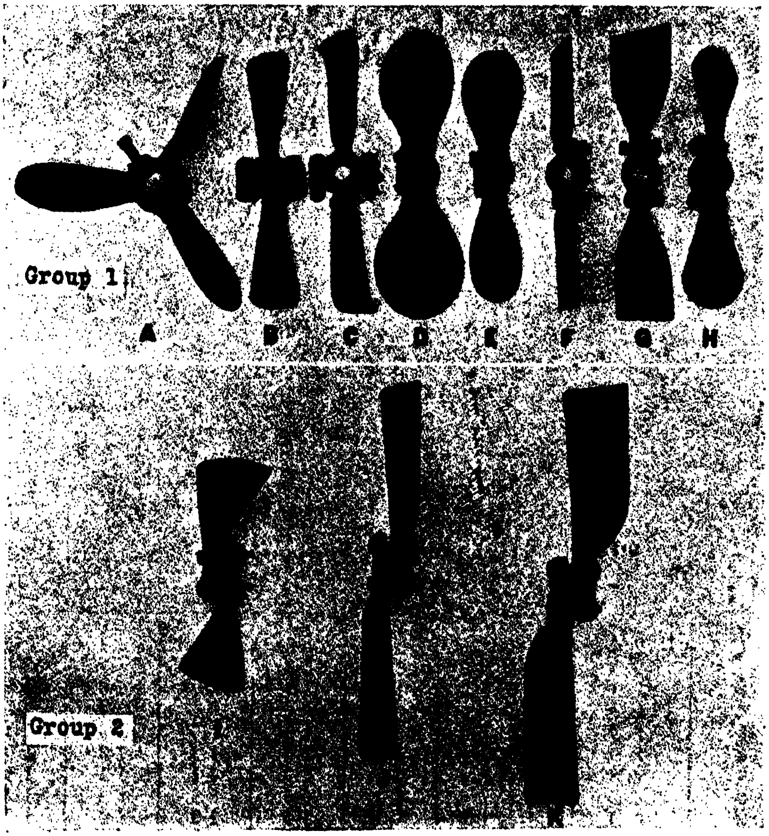

FIG. 55. Types of agitators employed in studies on the efficiency of emulsification (Smith).

Using a 200-gallon, half-round tank, with agitator speeds of from 100 to 300 r.p.m. and tank dimensions: length, 45 in.; width, 36½ in.; depth, 33 in., Smith investigated emulsification efficiency, using oils coloured with Oil Soluble Red. Examination of the discharging spray was made. Without the aid of an emulsifying agent, 2 gallons of kerosene were dispersed in 198 gallons of water (1 per cent. emulsion). With the exception of test 10 (see Table 46) the oil was added when commencing

TABLE 45

SPECIFICATIONS OF THE AGITATORS SHOWN IN FIG. 55

	Agitator.	Number of Blades.	Total Area of Blades.	Length of Blade.*	Pitch of Blade.
			sq. ins.	ins.	degrees.
Group 1	A	3	45	6½	60
	B	2	19	5¾	30
	C	2	31	6¼	60
	D	2	42	6½	35
	E	2	24	5¾	30
	F	2	28	6	90
	G	2	35	6½	50
	H	2	23	6	35
Group 2	I	2	22	5¼	30
	J	2	24	8½	30
	K	2	45	9¼	30

* Centre of shaft to tip of blade.

to fill the tank and the agitator was run without interruption until the tank was filled and emptied.

TABLE 46

RESULTS OF TESTS ON AGITATOR SPEED MADE WITH 200-GALLON TANK, USING OIL AND WATER ONLY

Test.	Number and Type of Agitators.	Agitator Speed (r.p.m.).	Number of Gallons in Tank when Samples were taken.				
			200	150	100	50	10
			Per cent. of Oil in Samples.				
1	2 B	100	0·3	0·2	0·2	0·2	7·5
2	2 B	200	0·5	0·7	1·0	1·1	1·4
3	2 B	300	1·0	1·0	1·0	1·0	1·0
4	2 D	100	0·3	0·7	0·9	0·7	2·7
5	2 D	200	1·0	1·0	1·0	1·0	1·3
6	2 D	300	1·0	1·0	1·0	1·0	1·0
7	4 B	200	0·9	0·9	1·1	1·1	1·1
8	4 D	100	0·6	0·6	0·8	0·8	1·4
9	4 D	200	1·0	1·0	1·0	1·0	1·0
10*	2 D	200	1·0	1·0	1·0	1·0	1·0

* Oil added when tank was filled, and agitator run for 2 minutes prior to first sampling.

"The data show that with only two small agitators in the 200-gallon tank a uniform mixture was produced and maintained by a speed of 300 r.p.m. In regular sprayer equipment there would be four such agitators in a 200-gallon tank. The test with the four small agitators shows practically a uniform mixture at a speed of 200 r.p.m. Two large agitators produced insufficient agitation at a speed of 100 r.p.m., but they gave a uniform mixture when the speed was increased to 200 r.p.m. It is interesting to note that even four large agitators failed to produce a uniform mixture at a speed of 100 r.p.m., indicating that increased speed is more important than an increase in the number of agitators." Other experiments confirmed that high-speed agitation is essential for oil sprays, because the oil tends to concentrate at the surface of the tank mixture and only violent agitation will effectively draw this oil down to the bottom of the tank."

An experiment with another tank of 465 gallons capacity, using agitators with speed of 210 r.p.m., showed that four large agitators (type D) were more efficient than seven small agitators (type E). "An equipment which would give satisfactory agitation in one tank might give less satisfaction in another, the agitation being either more than required or less than required." The presence of an emulsifying agent greatly facilitates the production and maintenance of a uniform dispersion.

Smith now investigated the important question of the power consumption in making emulsions with different agitators. A 300-gallon tank was employed and the blades of adjacent agitators were either at right angles to one another or the axes of the blades were parallel and the agitators paired according to the pitch of the blades, in which case the agitators of each pair throw the water toward each other. The latter position is known as the parallel position. Table 47 from Smith's report collects the data on power consumption.

TABLE 47

HORSE-POWER REQUIRED TO OPERATE AGITATORS IN TESTS MADE WITH A 300-GALLON TANK

Series of Test.	Approximate Speed (r.p.m.).	Kind and Number of Agitators.	Position of Agitator.	Quantity of Water in Tank (gallons).	Power required to Agitate (h.p.).
1	100	4 D	Right angles	300	0·08
	200	4 D	Right angles	300	0·43
	300	4 D	Right angles	300	1·76
2	100	4 D	Parallel	300	0·15
	200	4 D	Parallel	300	0·56
	300	4 D	Parallel	300	2·00
3	100	4 B	Parallel	300	0·06
	200	4 B	Parallel	300	0·15
	300	4 B	Parallel	300	0·65
4	100	1 E, 2F	Parallel	300	0·09
	200	1 E, 2F	Parallel	300	0·40
	300	1 E, 2F	Parallel	300	1·48
5	300	4 D	Parallel	100	0·92
	300	4 D	Parallel	200	1·92
	300	4 D	Parallel	300	1·98

There is more efficient agitation, involving greater power consumption, when the agitators are in the parallel position. Larger agitators produce better agitation than smaller ones. From test 5, varying the quantity of water in the tank, it is apparent that there is no material decrease in the power consumption until the tank is about half empty.

In considering mixing vessels or tanks it should be pointed out that they possess one great advantage, although they operate on individual batches. They permit the whole of the bulk of continuous medium to be present before introducing with agitation the phase to be dispersed. It is, as a rule, eminently desirable to run the disperse phase into the external phase, so assisting mechanically the promotion of the type of emulsion demanded by the emulsifying agent used and which is in solution or suspension in the external phase. Experience has amply proved the efficacy of the slow admission of the disperse phase during agitation, and for concentrated emulsions this is absolutely essential.

A vexed question concerns the practice of dividing the external phase into two portions, one to be added later to dilute the otherwise finished emulsion. The present writer's opinion is that, in technical operations, the whole of the continuous medium should be employed from the commencement, as the dilution of a concentrated emulsion often proves difficult.

By dividing the continuous medium, a more concentrated initial solution of the emulsifying agent is possible, and, as some experiments by Sumner[1] have shown, by increasing the concentration of emulsifying agent (soap), there is a continuous downward trend for the mean radius of the benzene globule. Although the range of size is not appreciably reduced, it is shifted as a whole. Thus :—

Soap concn.	Per cent. of Total Mass of Globules of Radius (in μ).								
	2—2·5	2·5—3	3—3·5	3·5—4	4—4·5	4·5—5	5—5·5	5·5—6	> 6
0·0005 M . .	—	—	—	13·5	22·5	30·5	17·5	9	7
0·0010 M. . .	—	—	4·5	21·5	33·5	23	12	5·5	—
0·0015 M . .	—	5	22	20	30	14	9	—	—
0·0020 M . .	—	18	24	29·5	17·5	10·5	—	—	—
0·0025 M . .	5·5	28·5	38·5	13	12	2·5	—	—	—

These results were obtained by dispersing the benzene (as vapour from a jet) below the surface of the soap solution. Where agitation is employed in mixing the liquids, it seems self-evident that a new degree of agitation will be necessary if the continuous phase is reduced in volume.

Experience convinces that the phase-volume ratio factor plays an important *rôle* in emulsification,[2] though in certain cases the nature and/or the concentration of the emulsifying agent may outweigh this. Here, as in nearly all instances of technical emulsions, each system demands individual consideration.

THE AIR/LIQUID INTERFACE FACTOR

According to a patent granted to Imperial Chemical Industries, Ltd. and Clarke,[3] the constituents of an emulsion are sprayed through at least two nozzles so as to impinge on each other or on a common surface; at least one of the nozzles is multiple so that a motive fluid such as steam or compressed air may be used, and partly-mixed materials are lifted back into the spray. Thus, linseed oil may be sprayed by steam and at the same time ammonium oleate solution sprayed by compressed air.

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[1] *J. Phys. Chem.*, **37**, 279 (1933).

[2] Experimental evidence is given by Stamm and Kraemer, *ibid.*, **30**, 998 (1926); see also Weichherz, *Kolloid-Z.*, **47**, 133 (1929); Woodman, *J. Phys. Chem.*, **33**, 93 (1929).

[3] Brit. 331,928 (1929).

Hunter and Nash[1] point out that "the application of mixing jets to the contacting of two liquids is a development of rapidly increasing importance. Their efficiency combined with low cost and small back pressures all favour their adoption for this purpose." No quantitative work on the efficiency of jet mixing of liquids for emulsification, however, seems to have engaged attention.

A preliminary communication from Rogowski and Söllner[2] deals with the importance of the gas phase for the formation of emulsions. Preparing emulsions by shaking or by employing ultrasonic waves, they observed very pronounced differences in the ease of formation and the subsequent behaviour of the emulsions according to the presence or absence of air during emulsification. Thus with the systems toluene/sodium oleate solution, and toluene/sodium nitrate solution + the solid emulsifying agent, $CaCO_3$, the importance of a gas phase was noted. The nature of the gas apparently did not matter (see p. 363).

Similar results have been reported by Kremnev,[3] who prepared emulsions by the aid of a bubble method. If mercury and a second liquid be placed in a cylinder and air be bubbled through the lower (mercury) liquid layer, half-spheres appear on the mercury surface ("elementary mercury foam"). With a sufficiently powerful air stream, mercury-coated bubbles rise through the upper liquid to the air/liquid boundary. There the bubbles grow thinner, the heavy mercury becoming pendent and the gas portion lenticular. Eventually, the bubbles burst and a poly-disperse mercury emulsion results (see Fig. 56).

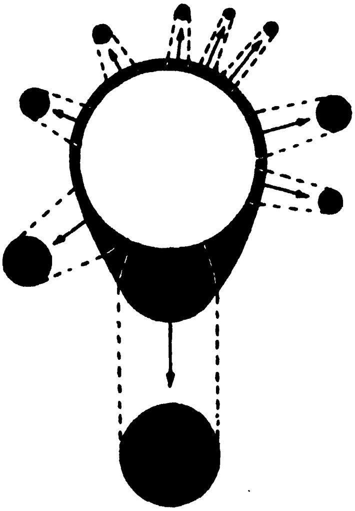

FIG. 56. Bursting of mercury-coated bubbles to yield a poly-disperse mercury emulsion (Kremnev).

Kremnev then investigated four systems varied in respect to the disposition of the liquids according to their densities :—

(1) $\dfrac{\text{Na oleate in water}}{\text{C Cl}_4}$.

(2) $\dfrac{\text{Benzene}}{\text{Na oleate in water}}$.

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[1] *Ind. Chemist*, 9, 313 (1933).
[2] *Z. physik. Chem.*, Abt. A., 166, 428 (1933).
[3] *Kolloid-Z.*, 68, 16 (1934).

$$(3)\ \frac{\text{Benzene solution of Ca oleate}}{\text{Water}}.$$

$$(4)\ \frac{\text{Water}}{\text{Benzene solution of Ca oleate}}.$$

Thus, the aqueous phase is the lighter in two cases and the heavier in two; the air stream commenced in the lower (heavier) liquid below the dineric interface.

In case (1) the air bubbles passed through the dineric interface to the free air boundary, where they burst. The result was a large drop of CCl_4 and several smaller drops, often visible to the naked eye. The life of the drops was quite long,[1] and the emulsion was of the O/W type.

Sometimes the bubbles on bursting led to lenses of dispersed phase hanging below the air/liquid boundary, and these lenses gradually coalesced to a larger lens with its convex surface exposed to the soap solution. With 2·5 per cent. sodium oleate solution the diameter of the lenses reached 1·5—2 cm. When the mass of the lens was sufficient a large drop of liquid was torn away and sank.

In case (2) the aqueous soap solution was the under layer and the air bubbles commenced below its surface. These bubbles soon burst when reaching the benzene/air boundary, water drops of different mass sinking. The stability of the drops of the aqueous phase was very small, as the soap does not stabilise a W/O system.

In case (3) the aqueous foam led to a stable W/O system, and in case (4) there resulted an unstable O/W emulsion, as calcium soaps do not promote such emulsions.

Kremnev's investigations obviously concern a one-sided method of preparing emulsions (cf. Hatschek's transpiration method), although the phenomena involved may be included in the phenomena accompanying the preparation of emulsions by violent agitation.

At first sight, contrary to the foregoing statements, must be mentioned the fact that certain emulsions, seemingly of pronounced stability, may be broken by creating a foam at their free surface. This highly-interesting phenomenon of colloid physics is familiar in the churning for butter and in the use of the Gardiner mobilimeter for testing the stability of mayonnaise.

The subject has been more fully treated in the section dealing with milk (see p. 29). The present evidence definitely points to the creation of an air/liquid interface being unfavourable to emulsification,[2] when the emulsifying agent preferentially accumulates at that interface and/or there undergoes a change in character, such as denaturation in the case of egg proteins. With certain types of technical machines splashing, whipping or impinging on a solid surface unavoidably create an extended air/liquid interface. The marked difference in the performance of colloid mills entraining air and homogenisers which do not entrain air lends emphasis to this aspect of emulsification. Reference should be made to the investigation of Sibree [1] in this connection.

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[1] Cf. Rehbinder and Wenström, *Kolloid-Z.*, **53**, 145 (1930).

[2] Hall and Dawson, *Ind. Eng. Chem.*, **32**, 415 (1940), have experimentally verified that it is better to project the internal phase below the surface of the external phase.

PHYSICS OF EMULSIFICATION

The actual mechanism of emulsification is extraordinarily complex. Agitation of the two liquids breaks them into drops and cylinders, and a cylinder of liquid is unstable when its length exceeds $3\frac{1}{7}$ times its diameter. It then breaks into globules, the distance between the centres of the globules being that of the circumference of the cylinder.

Taylor [2] has deduced an approximate expression connecting the size of the largest globule that can exist in a fluid which is undergoing distortion at a given rate with the surface tension of the globule and the viscosities of the two liquid phases. The turbulence existing in an emulsifying machine, however, would greatly complicate the question of its verification. However, this author has dealt with the theory of the formation of emulsions in definable fields of flow.[3] He has discussed the distortion of a drop of one liquid by the viscous forces associated with certain mathematically definable fields of flow of another liquid surrounding it. An expression was found for small distortions from the spherical which occur at slow speeds. If L = the greatest, and B = the least diameter of the drop, then $(L - B)/(L + B) = F$ approximately, where F is a non-dimensional quantity, proportional to the speed of flow, which involves the interfacial tension, the viscosity and the radius of the drop.

Drops of oils of various viscosities were suspended in a sugar syrup, diluted with water to suitable viscosities. Two experimentally convenient fields of flow were studied, represented by simple mathematical equations :—

$$u = Cx,\ v = -Cy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$u' = \alpha y',\ v' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The first case, wherein the stream lines are rectangular hyperbolas, was realised by using four rollers, each pair rotating in opposite directions and the two rollers in each pair rotating in opposite directions. The second case was realised by two parallel bands which could be driven at variable speeds in either direction and in any desired ratio. The behaviour of the drops was registered photographically.

The author's results show that when a drop suffers slight distortion from the spherical form due to the stresses in the viscous liquid in motion round it, such distortion depends solely on the instantaneous conditions. Elongation of the drop occurs in the direction along which lines of particles are elongating at the greatest rate. For the four-roller apparatus, the long axis of the drop is horizontal (Fig. 57), while in the parallel-band apparatus it is at ·45 degrees to the bands. The slightly deformed drop has a shape which agrees with that deduced theoretically, when :—

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[1] *Trans. Faraday Soc.*, **27**, 161 (1931).
[2] *Proc. Roy. Soc.*, **A. 138**, 47 (1932).
[3] *Ibid.*; **A. 146**, 501 (1934).

$$\frac{L - B}{L + B} = \frac{19\eta' + 16\eta}{16\eta' + 16\eta} F$$

where η and η' are the viscosities of the syrup and oil respectively.

Elongation of the drop follows increase in the viscous drag on the surface of the drop, but the shape does not now depend on the instantaneous conditions of flow ; the two types of apparatus produce different effects. The final fate of the drop as the speed of distortion of the outer liquid increases greatly depends on the ratio η'/η. For very small values of η'/η, *e.g.*, 0·0003, the drop is still coherent, even though it becomes very long and narrow in both types of apparatus.

As the viscosity of the oil constituting the drop increases, the speed required to burst it becomes less with both kinds of flow. When $\eta'/\eta = 20$, the two kinds of disrupting field exert very different effects. In the four-roller apparatus the drop bursts at $F = 0{\cdot}28$, whereas the parallel-band apparatus, even at its highest speed, fails to burst the drop, which, in fact, attains a constant shape which depends only on η/η'.

Finally, Taylor mentions that : "It is remarkable that in the parallel-band apparatus the ease with which the drop can be burst increases as the viscosity of the drop rises from small values to be equal to that of the surrounding medium, but when the viscosity of the drop rises to several times as great as that of the outer fluid, the viscous drag of the latter is incapable of bursting it, however big the viscous stresses may be. The drop merely rotates, remaining nearly spherical.

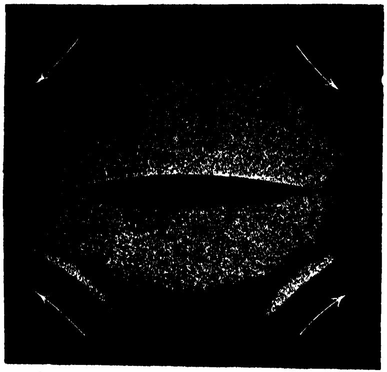

FIG. 57. Form of a drop which has been maintained symmetrically in the middle of the field for a time sufficiently long to ensure that the drop and surrounding fluid reached a steady state. One-quarter of each of the four rollers is shown in the corners of the photograph, and the direction of rotation of each is shown by means of an arrow (Taylor).

"The manner in which the drops burst is of interest. The act of bursting is always an elongation to a threadlike form. When this thread breaks up, it degenerates into drops which are of the order of 1/100th of the size of the original drop (see Fig. 58). This seems to be related to the known fact that when an emulsion is formed mechanically it contains drops which cover a very large range of sizes."

Important mathematical studies by Tomotika[1] followed Taylor's publications. Firstly, was discussed the instability of a long cylindrical column of an incompressible viscous liquid surrounded by a second viscous fluid under the action of both surface tension and viscous forces, both fluids being at rest. Theory and observation agreed that if the ratio of viscosities of the two fluids is neither zero nor infinity, the maximum instability invariably occurs at a certain definite value of the wave-length of the assumed initial varicosity so that the formation of drops of definite size would be anticipated. Taylor's experiments seemed to show that the flow in the fluid environment exerts some stabilising effect to inhibit the formation of drops until there has resulted considerable reduction of the thread. The drops which are ultimately formed correspond in the newly formed cylindrical thread to varicosity of very short wave-length, which is initially stable ; as the oil thread is drawn out by the motion of the surrounding syrup its wave-length increases until it equals the circumference of the thread and then becomes unstable.

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[1] *Proc. Roy. Soc.*, A. **150**, 322 (1935).

Secondly, attention was devoted to a long, straight cylindrical column with uniform small circular cross-section of a viscous liquid environed by another viscous liquid, assuming that the thread and surrounding fluid are being stretched at a uniform rate and that the effects of inertia of the fluids are insensible and negligible in comparison with those of viscosity. Symmetry about the axis of the thread is assumed and only disturbances which are simple harmonic with respect to the co-ordinate parallel to the axis were considered.

Investigating the effect of the flow of the surrounding fluid on the stability of small motions of the thread caused by the small disturbances, Tomotika [1] found that the effect of this flow is to limit the increase in any initial disturbance to a finite value. Thus, true instability does not occur when the drop is surrounded by the field of flow which causes a drop to pull out into a cylindrical thread. On the other hand, disturbances formed at various stages in the process of drawing out can increase in very different proportions. Thus, varicosity which begins as soon as the cylindrical thread is just formed from the initial drop can only increase in relative amplitude in the ratio 1 : 20·89, but varicosity which forms when the cylindrical thread has been drawn out to ⅛th of its initial diameter can increase in relative amplitude in the ratio 1 : $2{\cdot}26 \times 10^{10}$. This seems to explain why the thread does not immediately break up into drops, but remains cylindrical until it has extended sufficiently to form drops which are about 1/1000th of the volume of the initial drop.

FIG. 58. Elongation of a drop to a thread which seems quite stable, but which gradually breaks up into a number of small drops spaced at nearly regular intervals when the apparatus is stopped (Taylor).

Oka,[2] at the suggestion of Tomotika, investigated the character of the equilibrium of a toroidal mass of liquid under the action of surface tension. His paper : " On the Instability and Breaking up of a Ring of Liquid into Small Drops," opens with the well-known fact that if a small drop of ink is placed on the still surface of water, it begins to sink and the form is gradually flattened and ultimately changes from the original spherical shape to a small horizontal circular ring. As this ring descends through the water, its radius progressively increases until the ring becomes unstable and varicose, showing the tendency to the production of bead-like swellings and contractions along the circumference of the ring. A series of drops of a uniform size will then result, under favourable conditions at nearly equal distances along the circumference.

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[1] *Proc. Roy. Soc.*, **A. 153,** 302 (1936).

[2] *Proc. Physico-Math. Soc. Japan,* **18,** 524 (1936).

Oka's analysis shows that maximum instability of a circular ring of liquid under the action of surface tension occurs in all cases at a certain definite value of the wave-length of the varicosity, indicating that drops of definite size would be formed, and this wave-length varies with the ratio of the radius of the ring to that of the cross-section. In other words, the number of drops into which the ring is broken up increases as the ratio of the radius of the ring to that of its cross-section increases.

Tomotika [1] now investigated the stability or instability of a long cylindrical column of a perfect fluid surrounded by another perfect fluid, taking account of the effects of inertia of the latter fluid which extends to infinity. He showed that the effects of inertia of the surrounding fluid on the mode of maximum instability of a liquid column are negligibly small when the density of the surrounding fluid is less than, or equal to, the density of the liquid inside the column, and that even when the former is a few times greater than the latter the effects are very small.

In a further paper: "Instability and Breaking up of a Ring of an Incompressible Perfect Liquid," Tomotika [2] re-investigated Oka's problem and developing statical and dynamical theories. In the statical theory the change of the surface area of the ring due to a small disturbance is first calculated, under the condition that the volume of the disturbed ring is the same as that of the undisturbed one, in accordance with the assumed incompressibility of the liquid. Thence, the upper limit is found for the number of drops into which a ring of liquid may be expected to be broken up by the action of surface tension, when the ratio of the radius of the cross-section to the radius of the ring is given.

In the dynamical theory, the potential energy of the disturbed ring reckoned from the undisturbed state and also the kinetic energy of the motion in the ring generated by a small disturbance are first calculated. An expression is derived which determines the mode of disintegration of the ring of liquid under consideration. Assuming various values for the ratio of the radius of the ring to that of its cross-section, the probable number of drops into which the ring is broken up is computed in each case.

Let the radius of an undisturbed ring be R and the radius of its circular cross-section be a. Deform the ring by giving a small disturbance of such a property that the cross-section of the disturbed ring remains circular and the radius R remains also unchanged. Then, a typical Fourier term of the disturbance may be represented by a varicosity with wave-length λ, in which the radius a' of the cross-section of the disturbed ring varies along the central line of the ring according to the law : $a' = a + \epsilon \sin m \phi$.

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[1] *Proc. Physico-Math. Soc. Japan*, **18**, 550 (1936).

[2] *Ibid.*, **18**, 535 (1936).

In this equation, ϵ is a small quantity, and m is a positive integer and is connected with the wave-length λ of the varicosity by the relation : $\lambda = \frac{2\pi R}{m}$. Now m evidently gives the number of swellings in the ring.

Putting $\alpha_* = \frac{R}{a}$, the ratio of the radius of undisturbed ring to that of its cross-section, then if $m > \alpha_*$ the surface area is increased due to the disturbance and, therefore, since the surface tension has the effect of decreasing the surface area, the equilibrium of the ring is stable with respect to the said disturbance.

On the other hand, if $m < \alpha_*$, the surface area is smaller after displacement and the ring will depart, by the action of surface tension, more and more from its original undisturbed equilibrium state, resulting in the final breaking up into drops. In this case the number of drops is given by m and the number of drops into which a ring is broken up is at most equal to α_*.

Tomotika summarises the results in the statical theory thus. The undisturbed state of a ring is :

$$\text{stable when } m > \alpha_*$$

$$\text{unstable when } m < \alpha_*$$

Introducing the wave-length λ of the varicosity the equilibrium is :

$$\text{stable when } \frac{2\pi R}{\lambda} > \frac{R}{a}, \textit{ i.e.}, \text{ when } 2\pi a > \lambda,$$

$$\text{unstable when } \frac{2\pi R}{\lambda} < \frac{R}{a}, \textit{ i.e.}, \text{ when } 2\pi a < \lambda.$$

In discussing the dynamical theory a necessary calculation involves the potential and kinetic energies of the motion caused in the ring of liquid by a small initial disturbance, assuming that the cross-section of the ring is always circular as in the statical theory and that the radius R of the ring is unchanged by the disturbance. Then an equation of motion is derived. It is shown that in accordance with the results of the statical theory the original undisturbed state of the ring is stable or unstable according as m is greater or smaller than α_*. The number of drops generally increases as the ratio α_* increases, *i.e.*, the smaller the radius of the ring itself, the more is the number of drops into which the ring is broken up. Table 48 shows the relation in question, confirming Oka's results and being in good agreement with observation.

TABLE 48

$\alpha_* = R/a$	5	6	7	8	9	10	11	12
Number of drops .	3	4	5	6	6	7	8	8

Employing the readily-dispersible cresoap emulsions of petroleum oils in water, Young [1] has made microscopical observations on the formation of emulsions. As soon as the cresoap miscible oil touched water, jets of oil streamed through holes in forming interfaces and dispersed myriads of oil globules in the water. The main interfaces undulated and made knobs that shed spheres of emulsion in the oil and water. Vertically rolling cylindrical currents in oil beside main interfaces and oppositely rotating pairs of horizontal currents in oil and water beside main interfaces drove liquids through the interfaces. Light Green SF dissolved in

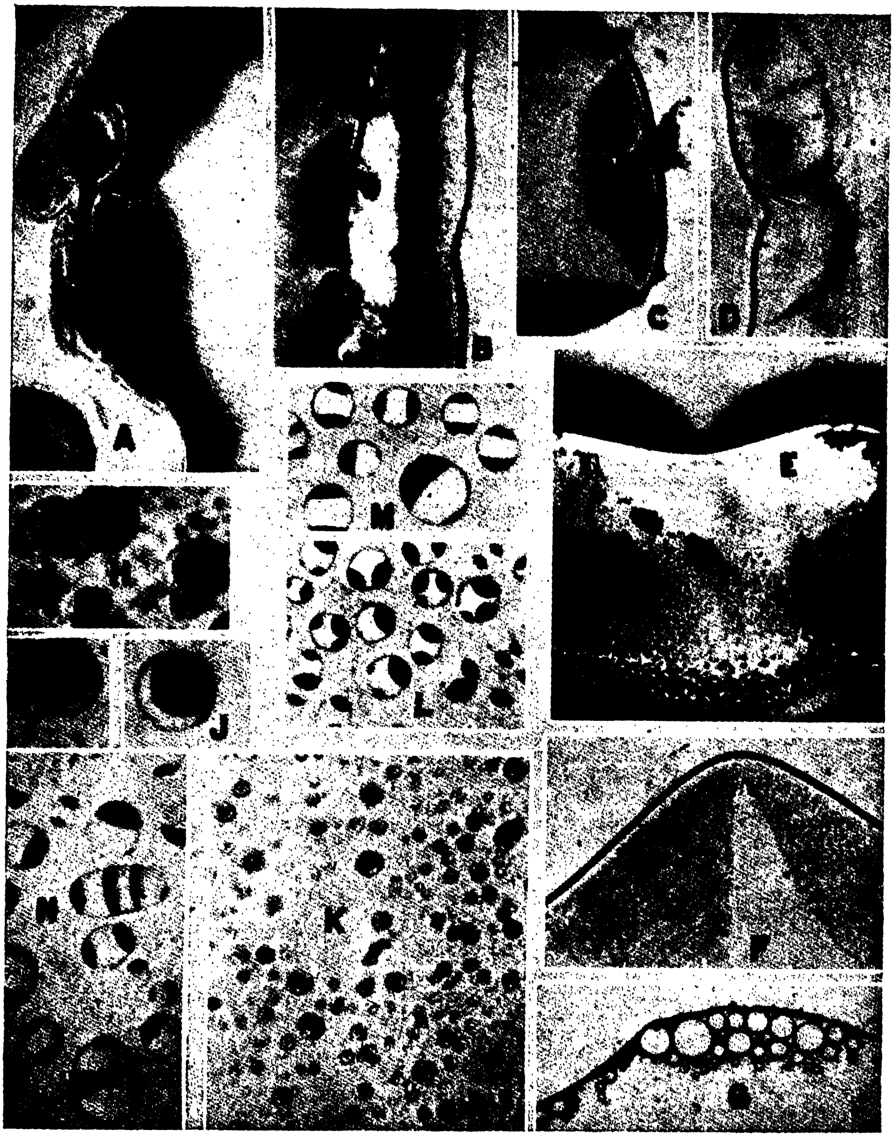

Fig. 59. See opposite page for legend.

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[1] *Trans. Am. Microscopical Soc.*, **55**, 260 (1936).

the water facilitated observation of emulsification. Similar phenomena occurred when methylene blue was substituted for Light Green SF, except that cresoap from the oil united with methylene blue and formed blue spheres dispersed in both oil and water. These blue spheres enclosed spheres of oil and water, and were enclosed in oil globules. These observations showed how globules of oil and emulsion are dispersed in emulsions in which artificial agitation makes innumerable interfaces (see Fig. 59).

The addition of KBr broke the emulsions rapidly, vertical and horizontal currents being observed like those in the formation of the emulsions.

FIG. 59. Photomicrographs of emulsification phenomena of miscible oils. The main interfaces photographed as broad black lines.

A. Oil 4 containing cresoap on left side and water on the right side of the interface after 10 minutes of contact. Granular band in the upper left corner is a cylinder revolving vertically in the oil. Below it the oblong granular body is an aggregate mass of water. A pair of horizontal swirls dispersed oil globules in the water on right side of main interface. The black sphere with a white centre is an air bubble. × 20.

B. Oil 36 containing Oil Red 0 and cresoap on left side, and water containing Methylene Blue on right side of main interface after 10 minutes of contact. Two pairs of horizontal swirls emulsified lenticular masses of water spheres in the oil. Across the interface, dim pairs of horizontal swirls emulsified strata of globules of oil and Methylene Blue with cresoap. × 20.

C. Like B, but showing two pairs of horizontal swirls in oil beside main interface, after 30 minutes of emulsification. × 20.

D. Oil 24 containing Oil Red 0 and cresoap on left, and water containing Methylene Blue on right side of main interface, after 5 minutes of emulsification. Pairs of horizontal swirls emulsified globules of oil and Methylene Blue with cresoap in the water. × 20.

E. Like B, with pair of horizontal swirls in oil at top, and dim pair of horizontal swirls in water below main interface, after 30 minutes of emulsification. At bottom, stratum of globules of oil and Methylene Blue enlarged by coalescence. × 20.

F. Like D, but showing pair of horizontal swirls in the oil after 5 hours of emulsification. Much water is dispersed in the oil. × 36.

G. Like D, but showing oil globules in the water below the interface, after 5 hours of emulsification. These oil globules did not coalesce with each other or the interface. Above the interface is a dense emulsion of water in oil. × 20.

H, I, J. Like B, but showing dispersed in water, typical globules of oil containing globules of Methylene Blue with cresoap. × 317.

K. Like D, showing dispersed in water globules of oil containing one or more globules of Methylene Blue with cresoap; emulsion 1 hour old. × 175.

L, M. Like B, showing oil-in-water emulsion 2 hours old. The oil globules had coalesced with others and had adhered to the coverglass; the inclosed Methylene Blue with cresoap had become lenticular bodies and bands. X 175.

N. Like B and L, but emulsion 3 hours old. Pressing on coverglass made these oil globules return to form shown in H. × 160.

A mathematical analysis of the mechanism of the subdivision of one phase into another has been made by Rossi,[1] who shows that the state of subdivision is affected mainly by the mechanical action of dispersing one phase into another, and but little by the physico-chemical properties of the emulsion that is already formed. Whilst interfacial tension facilitates the formation of the emulsion, it exercises but slight effect on the actual stability. Agreeing to this, the distribution of size of the globules is not uniform, but is subject to a statistical law. Rossi applies the statistical method of Boltzmann, and by calculations similar to those for the distribution of energy among the molecules of a gas, he derives a formula for the distribution of diameters.

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[1] *Gazz. chim. ital.*, **63**, 190 (1933).

Stamm and Kraemer[1] have published an important analysis of the mechanism of emulsification. The various means of agitating two liquid phases causes pulverisation of *both* phases, lamellæ and threads of one liquid into the other being formed. (Fig. 60 is a photomicrograph of a bitumen emulsion prepared by Mr. Iain Cameron ; owing to the working conditions the dispersed bitumen was exceedingly viscous, with the result that the bitumen lamellæ are clearly seen.) Such lamellæ break up into globules. The phase-volume ratio and the viscosities and densities of the two phases decide the extent to which the respective liquids disrupt one in the other. Coincident with and following upon the disruption process is the directly opposite process of the reunion of globules or masses of that phase which will constitute the external phase or continuous medium. The rate of such reunion will depend on the densities, viscosities and volume ratio of the two liquids and on boundary tension forces. Accurate specification of these is rendered impossible in face of the turbulence and the engendered complex hydrodynamical forces involved. Emulsion formation is obviously fostered by one liquid being more intimately subdivided and/or by the other liquid being the more easily coagulated to a bulk phase. In the absence of an emulsifying agent the rapid reunion of both liquids is always observed and separation into bulk phases occurs.

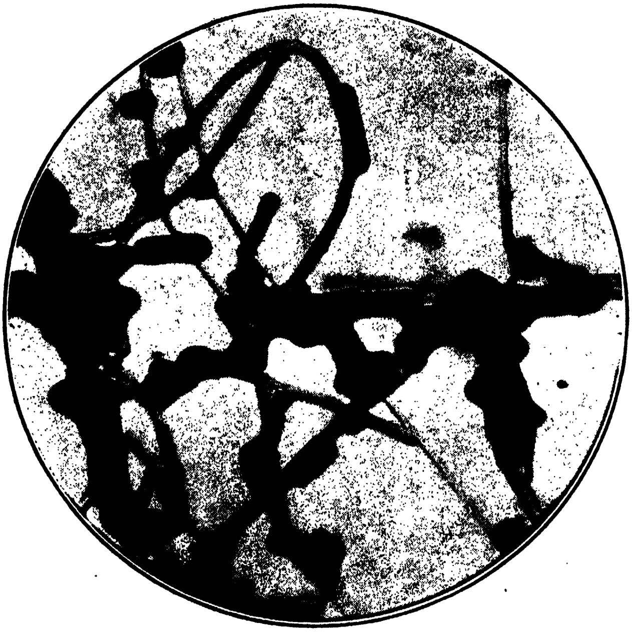

FIG. 60. Primary thread forms in emulsification : × 1000 (Cameron).

Low-melting alloys, such as Woods metal, lend themselves admirably to the investigation of the subdivision of one liquid in another. Clayton

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[1] *J. Phys. Chem.*, **30**, 992 (1926).

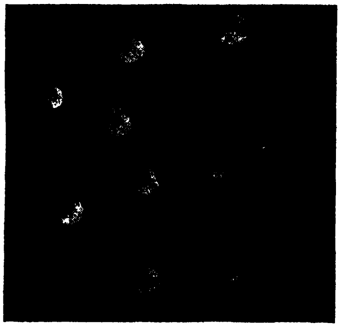
1. Distortion Prior to Globule Formation.

2. Multiple Globule Formation.

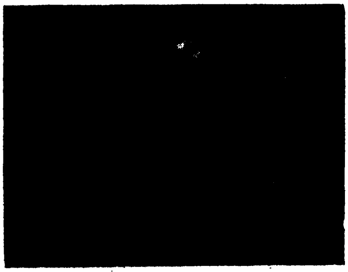
3. Elongated Globules Prior to Subdivision.

4. Subdivision.

5. Globules Immediately after Subdivision.



6. Globules Assuming a Spherical Form.



7. Final Form.

Fig. 61. Stages in dispersion to globules

and Morse[1] agitated the molten alloy with water and at intervals chilled suddenly the whole system. From the solidified particles of metal there could readily be picked out the various stages involved in dispersion (Fig. 61).

The ultimate stability of an emulsion depends on several factors. Enhancing stability will be: (1) fine dispersion of the globules, (2) a minimum difference in the densities of the two phases, (3) a viscous continuous phase, and (4) a stable film around the globules. For the last factor, time may be necessary to permit adequate adsorption of the emulsifying agent, accompanied in some cases by de-solution due to denaturation. We are led immediately to the conclusion that a given emulsifying agent plays two parts: (1) it permits easy dispersion owing to a reduced interfacial tension, and (2) it may promote stability after its adsorption, assuming the absence of disturbing factors such as chemical change or such physico-chemical alteration as leads to syneresis.

Reduction of interfacial tension should render emulsification easier. No thorough investigation seems to have been made of the power consumption involved in dispersing one liquid in another, in relation to the factors of interfacial tension, viscosity, density, and the type of agitation employed. Such a study is urgently needed, the data being correlated with size-frequency analyses.

Since the presence of an emulsifying agent must complicate both the pulverisation and the reunion stages in emulsification, it is agreed with Stamm and Kraemer that "it does not seem safe to assume that the mechanics of dispersion can be preserved uniform for comparison purposes, with the use of various emulsifying agents."

SUMNER ON THE CONDENSATION PROCESS

In view of the absence of disturbing factors incurred by mixing, shaking, agitating, grinding, etc., and since the air/liquid surface tension effects do not rise, the method of Sumner, already discussed, deserves special consideration as to the probable mechanism of emulsion formation under his relatively simple conditions. At the request of the present writer, Sumner has presented the following brief summary of his theory:—

Emulsification brought about by condensation of one component from the vapour phase may be explained most satisfactorily by postulating the formation and growth of nuclei from molecules in direct contact with the liquid continuous medium. This brings the mechanism into line with condensation or crystallisation in super-saturated systems of other kinds, and condensation of the simplest example, a supersaturated vapour condensing to a liquid, reveals the factors involved.

The formation of a nucleus means the collision and union of a number of molecules to an aggregate having the properties of surface, and this involves the generation of surface energy which must be provided by the energy of condensation. Thomson showed that, in consequence of surface tension, the vapour pressure p_r over a curved liquid surface increases as the radius r diminishes; it follows that in a vapour having a supersaturation pressure p_r, a liquid drop of radius less than r will evaporate, a drop of radius r will be in equilibrium, and one of radius exceeding r will grow by condensation on its surface. It may be shown readily that the nett increase in free energy involved in forming a drop of any given radius x from an ideal vapour is :—

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[1] *Chemistry and Industry*, **1939**, 304.

$$W = 4\pi x^2 \sigma\left(1 - \frac{2}{3} \cdot \frac{x}{r}\right)$$

where σ is the surface tension of the liquid. This is a thermo-dynamical relation, and, therefore, refers to molecules in the mass, *i.e.*, its application to individual groups of molecules is limited to those possessing average energy. W becomes negative when $x > \frac{3}{2}r$, this representing the condition for production of nuclei from "average" molecules. Now a droplet having $x > r$ is capable of spontaneous growth, but since addition of work is required for a radius less than $\frac{3}{2}r$, the molecules giving rise to such a nucleus must possess energy above the average. Conversely, for molecules of less than average energy, the minimum radius of a nucleus will exceed $\frac{3}{2}r$.

At a given temperature, the probability P_n that a group of n molecules will be formed will increase with the vapour pressure p_r and n constant; for a definite value of p_r, P_n will diminish as n is increased. To each value of p_r two numbers may be assigned, where (1) n_1 is the least number of molecules in an aggregate, the probability for whose formation is less than a given very small quantity, and (2) n_2 is the number of molecules in an aggregate for which the nett change of free energy in condensation is zero, for molecules of any given energy. At low supersaturations n_1 is small and n_2 is large, so that nuclei will not be formed with the molecules considered. Whereas P_n and, consequently, n_1 increase with p_r, n_2 diminishes; n_1 and n_2 therefore approach one another until $n_1 = n_2$. Beyond this stage $n_1 > n_2$, so that nuclei derived from the given molecules will appear. The number of nuclei formed per second depends on P_n and the range n_2 to n_1; since P_n and n_1 rise and n_2 falls with increase of p_r, it will increase rapidly with supersaturation beyond the critical value.

The production of nuclei is, therefore, dependent on the existence of a degree of supersaturation which is related to the surface energy generated and to the energy of the molecules concerned. In Sumner's original paper (to which reference should be made for further details of this treatment) it was considered that molecules of average energy were of chief importance in the formation of a highly disperse system. As a generalisation this is probably incorrect, since there is reason to believe that an optimal range of molecular velocities exists for nucleus formation and the Maxwell average velocity is not necessarily within this range.[1]

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[1] Cf. Svedberg, "Colloid Chemistry" (1928), p. 53.

Nevertheless, it remains true that of the participating molecules, those having velocities nearest to the average will be most numerous, and, therefore, of chief importance. Similarly, the optimal size of a nucleus will be that nearest to the critical size and will diminish with rise of p_r.

In the method of emulsification described, a steady state is set up within a condensation zone in the neighbourhood of the jet, such that as much material enters per second in the form of vapour as leaves in the form of droplets. This corresponds with a definite degree of supersaturation of (oil) molecules relative to the medium. The growth of a nucleus depends on the rate of deposition of molecules on its surface and on the time of passage through the condensation zone. Now the rate of deposition is the nett result of the opposing tendencies of molecules to condense on or to leave the surface ; the former increases with supersaturation and the latter with decrease in the particle size. These considerations may be utilised to correlate the observed effects of mechanical factors such as the incoming pressure of the vapour and the size of the jet.

When the continuous (water) phase contains a surface-active solute such as sodium oleate, two effects contribute to a reduction in mean particle size. The interfacial tension between an oil droplet and the solution is reduced, so that the critical number n_2 falls and the range of group sizes available for nucleus formation is extended, irrespective of any change in the equilibrium supersaturation. On the other hand, growth of a nucleus by accretion of oil molecules is impeded by the adsorbed film of soap. The equilibrium within the condensation zone will, therefore, readjust itself to give a larger number of small particles, the conditions of injection being constant. The effect will be progressive with rise of soap concentration, as long as the effect of the latter on the interface does not reach a limiting value.

EMULSIFICATION BY ULTRASONIC WAVES

Experiments by Wood and Loomis[1] on the physical and biological effects of supersonic waves, and of Richards and Loomis[2] on the chemical effects of such high frequency compressional waves have been recently extended to the study of emulsification. The vibration of a piezo-electric quartz plate placed between two electrodes connected with an oscillator of high frequency produces inaudible sound waves of frequencies of the order 100,000—500,000 per second. The quartz and the electrodes are immersed in an oil bath. The intense sound waves travel up through the oil into any vessel suspended in it.

Richards[3] showed that when benzene and water are placed in a test tube which has been previously wetted with water and the tube is irradiated with sound waves of 300,000 cycles per second, the benzene phase immediately becomes cloudy, the water phase more slowly so and, eventually, the interface between the two liquids disappears.

He found that emulsification occurs primarily at the wall in contact with benzene and not at the dineric interface. Employing very low intensities of sound waves of the order of 30,000 cycles per second, in water-wetted tubes containing a water/benzene interface, the white cloud of emulsion proceeded from the walls of the tube slowly into the benzene layer only. The interface was only slightly disturbed and the water phase remained clear until, after two minutes, when the benzene phase had become extremely milky, a thin but gradually increasing cloud of emulsion drifted down from the interface.

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[1] *Phil. Mag.*, **4**, 417 (1927). U.S. 1,734,975 (1929).

[2] *J. Am. Chem. Soc.*, **49**, 3086 (1927) ; cf. Marinesco, *Compt. rend.*, **196**, 346 (1933) ; Marinesco and Holtz, Fr. 844,009 (1939).

[3] *J. Am. Chem. Soc.*, **51**, 1724 (1929).

Employing dried test tubes into which water was pipetted with such care as to prevent wetting the upper part of the tube, benzene being then similarly added, emulsification was entirely absent unless the intensity of the sound waves was so great as to agitate the interface considerably. An emulsion then formed at the wall-layer so produced, and was slowly driven through the liquid by radiation pressure. Whenever drops of water were attached to the wall opposite the benzene layer, they became milky and gradually emulsified completely. The converse was also true.

Richards states that these and other observations indicate clearly that emulsification in a liquid occurs mainly at the walls of the containing vessel when they are wetted with the liquid dispersed. This makes it improbable that compressional waves in the liquid produce the action; more probably, the transverse waves in glass (noted by Wood and Loomis) are the effective agents. In all cases where sound is transmitted through a glass vessel into a liquid, transverse waves must be considered as a possible primary explanation for any effects observed.

Freundlich and his co-workers have been prominent in research in this field. Bull and Söllner[1] dispersed mercury in water and aqueous solutions, obtaining coarse heterodisperse emulsions with globules whose average diameter lay between 1 and 2 μ. Dispersion was favoured by electrolytes of high valency and easily adsorbed ions, notably ammonium citrate and vucine hydrochloride. Emulsification of mercury was also secured easily with viscous, oxygenic liquids like olive oil and turpentine; very feeble dispersion occurred in benzene, toluene and CCl_4.

It is, however, with the mechanism of emulsification that recent investigations have been concerned. Freundlich[2] has summarised the present position, emphasising the importance of the gas phase. Ultrasonic dispersion does not occur *in vacuo*, or a very poor emulsion forms which breaks immediately. The nature of the gas is of no account. He points out, too, that there seems to be a limiting concentration of the disperse phase (in the absence of emulsifying agents), a stationary state being attained; the sound waves now both make and break the emulsion. To demonstrate this effect an emulsion of benzene is placed in a thick-walled, capillary U-tube. "If the tube is dipped into the vibrating oil-bath, striations of beautiful regularity are formed after a short time, in both branches of the tube (Fig. 62). The droplets are gathered in the nodes, the antinodes in between often being absolutely clear. The distance between two nodes is equal to half a wave-length in the liquid." Removal of the tube from the bath is followed by short persistence of the striations and then sedimentation; currents in the liquid and Brownian motion destroy the orientation.

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[1] *Kolloid-Z.*, **60**, 263 (1932).

[2] "Technical Aspects of Emulsions" (London, 1935), p. 1. Sata has confirmed the significance of the gas phase; *Kolloid-Z.*, **71**, 48 (1935).

When an emulsion of high enough concentration is held for sufficient time exposed to the irradiation, there form in the nodes large drops which sedimentate in the bend of the U-tube. Freundlich believes that they are produced by an orthokinetic coagulation; the small globules which travel parallel from the antinodes to the nodes with different velocity are driven together and eventually coalesce. It is possible that near the walls of the tube there exist regions where the emulsion is destroyed and other regions where it is produced.

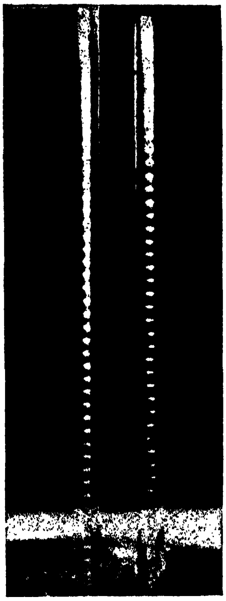

FIG. 62. Striations in emulsions subjected to ultrasonic vibration (Freundlich).

The striations formed probably are related to Kundt's method for determining the wave-length of sound waves, but the theory underlying this is yet incomplete.

Freundlich finally indicates that his results are not due to some specific property of the ultrasonic waves, since these merely serve as one method of introducing mechanical energy, perhaps better defined than ordinary shaking or stirring.

An important development in the explanation of the action of ultrasonic waves in producing emulsions is due to Bondy and Söllner,[1] who conclude that cavitation at the interface is the cause of emulsification. Cavitation is favoured by dissolved gases acting as nuclei, and the hydrostatic pressure exerted by gases is essential for the collapse of cavities. The same effect is shown when steam is allowed to condense in the interface: oil/aqueous soap solution, even concentrated emulsions being formed. (Note that air will not give the same efficiency.)

The cavitation caused by acoustic waves of sufficient energy probably forms during the dilatation stage. In contrast to usual technical emulsification, increasing the temperature of the two liquids detracts from the efficiency of emulsification by the aid of ultrasonic waves. Rise of temperature militates against cavitation.

Whilst cavitation is thus essential for emulsification between oil and aqueous systems, it is of no importance at all in the ultrasonic dispersion of mercury. This is the conclusion in a later paper by Bondy and Söllner,[2] who confirmed the findings of Richards. In agreement with the earlier results of Nordlund,[3] it is believed that the dispersion of mercury is due to the bursting of bubbles of the other liquid coated with thin films of mercury. The mercury emulsions are stabilised by adsorbed gases.

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[1] *Trans. Faraday Soc.*, **31**, 835 (1935).
[2] *Ibid.*, **31**, 843 (1935).
[3] *Kolloid-Z.*, **26**, 121 (1920).

Experimental proof of cavitation was given Söllner[1] when he investigated the formation of fogs, a single phase being irradiated and thus avoiding the opacity accompanying emulsions. When long columns of degassed liquids were irradiated by high energy, slightly glittering zones

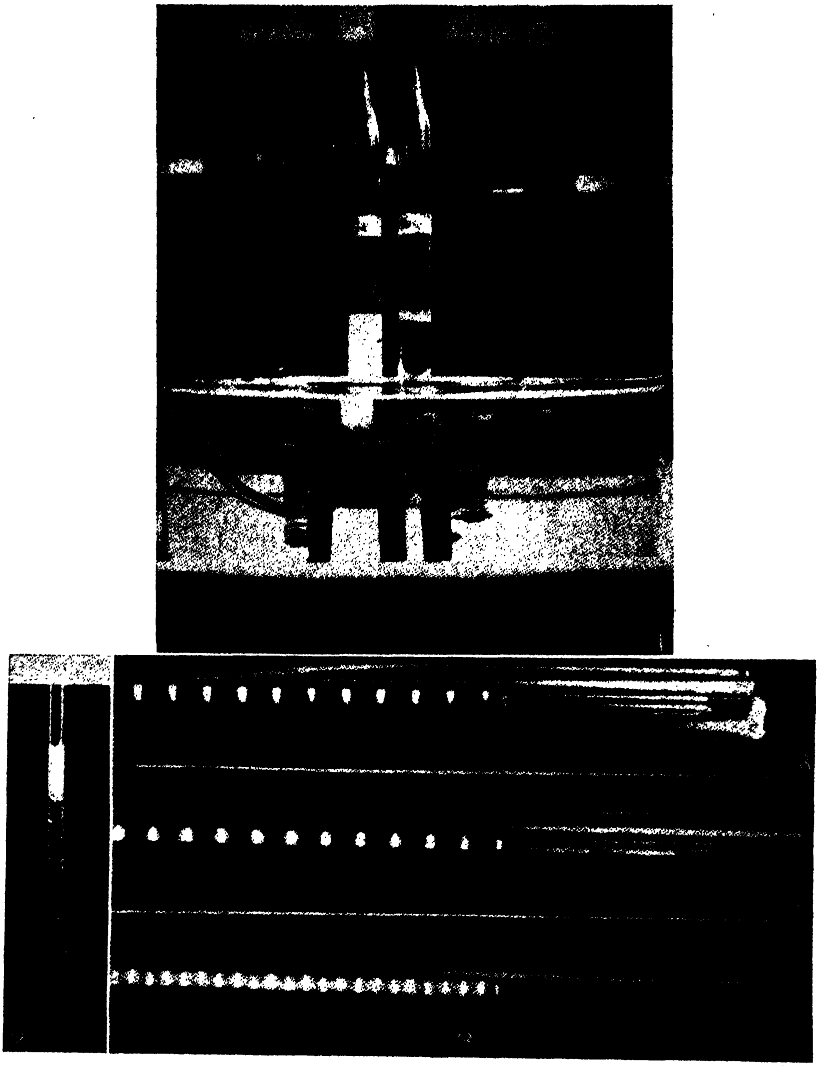

FIG. 63.

1. Emulsification by ultrasonics. The influence of the presence of a foreign gas upon emulsification. About one-third actual size.
2. Coagulation of an emulsion by ultrasonics. About one-quarter actual size.
3. Stationary wave patterns. (*a*) Toluene in water; (b) quartz in water; (c) toluene and quartz in water. About 1·5 times actual size.

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[1] *Trans. Faraday Soc.*, **32**, 1537 (1936).

of slight opacity, which disappear without producing gas bubbles, are formed in the liquid when it disrupts, due to the stretching by the ultrasonic waves.

An interesting paper by Bondy and Söllner [1] concerns quantitative experiments on emulsification by ultrasonic waves (see Fig. 63). Both W/O and O/W emulsions were investigated, as well as metal emulsions.[2] In the absence of emulsifying agents, the concentration of the internal phase soon reached a limiting value : the rate of emulsification becoming equal to the rate of coagulation. When dispersing toluene in water, this limiting value is 4·2 to 4·5 per cent. (by volume), when using high energies and it was reached in shorter time according to the degree of radiation. Although the rate of formation of emulsion increases strongly with increasing energy the rate of coagulation also increases. Again, with high energies the concentration decreases with extended time of radiation, attributed to the rise in temperature and to the degassing of the system.[3]

Added emulsifying agent assists dispersion and the concentration of the emulsion increases with increasing time of irradiation, approaching the maximum value of 50 per cent. first rapidly, then more and more slowly. With high energies toluene and 1 per cent. aqueous sodium oleate in equal volumes form an emulsion in 30 seconds. Gradual addition of further toluene undergoes rapid dispersion until the limit of about 75 per cent., after which the emulsion breaks, a thick layer of toluene appearing above the aqueous phase. The emulsion is very finely dispersed, but continued irradiation only coarsens the system.

Many mercury emulsions were studied. The marked influence of viscosity of the organic liquids (continuous phase) was demonstrated. In contrast to oils, feebly dispersed in highly viscous liquids, mercury emulsions are stabilised. Dispersing the metal in the homologous series of the aliphatic alcohols, the stability increases when ascending the series. Remarkable was the observation of much better emulsification in bromine derivatives when compared with closely related chlorine compounds, possibly due to some interfacial reaction. Rubber proved an excellent agent for mercury in many organic liquids.

A later communication by these authors [4] comprehensively examined the mechanism of coagulation of emulsions by ultrasonic waves. Separate treatment is accorded to the fundamentally different mechanisms of the emulsification of mercury and of organic liquids (" oils "). A most interesting discussion is summarised by the authors as follows.

" Radiation pressure " caused by diffraction of sound energy by the individual particles drives the latter to and fro, thus increasing the rate of spontaneous coagulation by a kind of orthokinetic coagulation. It accumulates the particles at the nodes (or antinodes), wherever stationary waves occur. Here rapid coagulation sets in, the orthokinetic (and spontaneous) coagulation being enormously accelerated by the high concentration at the nodal (or antinodal) zones of accumulation, the rate of coagulation by ultrasonics being mainly dependent upon the formation of the latter.

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[1] *Trans. Faraday Soc.*, **32**, 556 (1936). See also Söllner, *J. Phys. Chem.*, **42**, 1071 (1938).

[2] Previously studied by Marineau, *Bull. soc. roumaine phys.*, **36**, 181 (1934).

[3] A detailed account of degassing water is given by Paunov, *Ann. univ. Sofia. II. Faculté phys.-math.*, Livre 1, **35**, 179—205 (1938—1939).

[4] *Trans. Faraday Soc.*, **32**, 616 (1936).

In aqueous mercury emulsions the locus of coagulation may be readily separated from that of emulsification : coagulation proceeding in the interior of the aqueous phase, emulsification exclusively at the interface of large bulks of metal and water.

In aqueous emulsions of organic liquids this separation is not so easily effected. Both coagulation and emulsification (the latter due to cavitations) take place. At high energies close to surface and interfaces coagulation and emulsification counterbalance each other and cannot be separated. But in the interior of the liquid under suitable conditions stationary waves and zones of accumulation (and coagulation) may be observed. Emulsification needs an energy exceeding a certain limit ; coagulation may therefore be called forth exclusively below this limit, as well as by preventing cavitation (and therefore emulsification) if a sufficiently high external pressure is applied. The rate of accumulation at nodes (or antinodes) depends markedly on the particle size. With the wave-lengths used, it proceeds pronouncedly and rapidly with particles having a diameter above 1μ. Accumulation and coagulation are practically not observed with particles of truly colloidal dimensions.

In aqueous systems, particles less dense than the medium of dispersion are accumulated at the nodes, denser ones at the antinodes. Thus, in a system containing particles denser and less dense than the medium of dispersion the particles of different density may be separated from each other by irradiation with ultrasonics.

A mass of literature is now published dealing with ultrasonics as a new tool in research.[1]

The first industrial application in the field of emulsions is the SONIC OSCILLATOR for the treatment of milk and ice cream and for sonic bacteriolysis.

THE SONIC OSCILLATOR

This apparatus was primary designed for the production of soft curd milk [2] and is marketed by the Submarine Signal Company of Boston, Mass.

[1] Summaries are given by : Bergmann, " Der Ultraschall und seine Anwendung in Wissenschaft und Technik " (Berlin, 1937) ; Söllner, *J. Phys. Chem.*, **42**, 1071 (1938) ; Wannow, *Kolloid-Z.*, **81**, 105 (1937) ; Richards, *Rev. Modern Phys.*, **11**, 36 (1939) ; Schmid and Roll, *Z. Elektrochem.*, **45**, 769 (1939) ; Baumgardt, *Chimie et industrie*, **36**, 686 (1936) ; Hiedemann, *Chem. Weekblad.*, **34**, 390 (1937). Technique is described by : Fox and Rock, *Phys. Rev.*, **54**, 223 (1938) ; *Rev. Sci. Instruments*, **9**, 341 (1938) ; Porter, *Ind. Eng. Chem., Anal. Edn.*, **12**, 748 (1940) ; Freundlich, *Ind. Chemist*, **13**, 488 (1937) ; Freundlich and Gilling, *Trans. Faraday Soc.*, **35**, 319 (1939) ; Stäger, *Schweiz. Tech.*, **1938**, 113. Emulsion preparation is treated by : Rzhevkin and Ostrovskii, *Acta Physicochim. U.R.S.S.*, **1**, 741 (1934) ; Tumanskii, *Colloid-J.* (*U.R.S.S.*), **5**, 105 (1939). Physicochemical investigations are dealt with by : Sata, *Kolloid-Z.*, **81**, 182 (1937) ; Söllner, *Trans. Faraday Soc.*, **34**, 1 (1938) ; Freundlich and Söllner, *ibid.*, **32**, 966 (1936) ; Burger and Söllner, *ibid.*, **32** 1598 (1936) ; Sata and Naruse, *Kolloid-Z.*, **86**, 102 (1939) ; Schmid, *Z. Elektrochem.*, **44**, 728 (1938) ; Bergmann, *Brennstoff-u. Wärmewirt*, **21**, 151 (1939).

[2] The characteristics of soft curd milk are described in Clayton's " Colloid Aspects of Food Chemistry and Technology " (London, 1932), p. 280.

Chambers [1] has carried out pioneer work and he describes [2] the apparatus illustrated in Fig. 64.

The oscillator consists of a stainless steel diaphragm approximately 2 ft. in diameter which is vibrated electromagnetically at a frequency of 360 vibrations per second. A stainless steel cover is so arranged that it can be bolted against the diaphragm forming a chamber therewith. The milk to be treated is introduced into this chamber through the inlet opening at the outer edge of the cover and in order to pass out of the chamber must of necessity flow over the centre of the diaphragm where it is subjected to the intense vibration of the latter before passing out through the centrally located outlet opening in the cover. A water jacket on the back of the unit is connected to the cold water supply and cools the electrical windings and magnetic circuit. To operate the oscillator a 180 cycle alternating current is required. The unit handles about 250 gallons per hour, the power consumption being 5½ h.p.

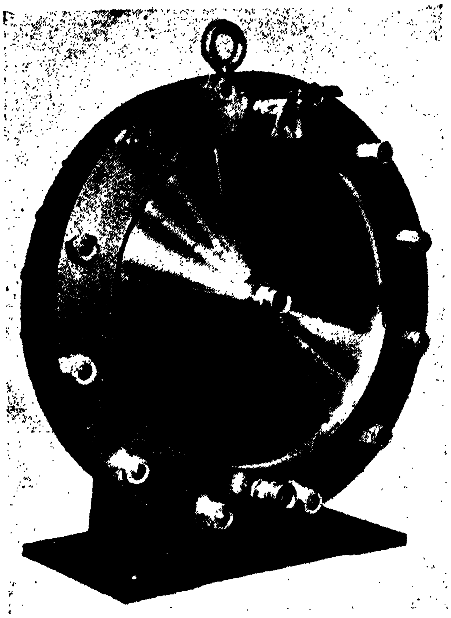

FIG. 64. The sonic oscillator.

The application of ultrasonic waves to the making of mayonnaise has been patented by Freedman.[3] Agitation of the various ingredients is replaced by oscillations of piezo-electric crystals contained in a long inclined duct, egg, oil and vinegar being added at different points.

RULE OF THE DISPERSED PHASE

Brief mention must be made of Wo. Ostwald's *Bodenkörperregel.* His first communication [4] (on gels) showed that in contrast to ordinary solutions of molecularly-dispersed substances, colloidal "solubility" (peptisation) is *not* independent of the quantity of the phase which undergoes dispersion. Frequently colloidal solubility increases as the quantity of the dispersed phase is increased, probably reaching a solubility maximum or peptisation optimum. Further increase in the quantity of the dispersed phase leads to decreased peptisation. The simple explanation was advanced that the dispersed phase absorbing the peptising agent and thus peptisation itself would pass through a maximum. Experiments by von Buzágh [1] on the peptisation of $BaCO_3$, casein, dyes and iron hydroxide, and by Ostwald, Steinbach and Köhler [2] on coarse suspensions, supported Ostwald's contention.

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[1] Chambers and Gaines, U.S. 1,992,938 (1935). See also Williams, U.S. 2,170,178 (1939); Can. 358,301 (1936); Submarine Signal Co., Brit. 458,872 (1936); Ashton, Ger. 666,097 (1938); Williams, U.S. 2,138,051—2 (1938); Hiedemann and Brandt, Fr. 828,204 (1938); L'Auxiliaire des chemins de fer et l'industrie and Austerweil, Fr. 841,359 (1939).

[2] *Food Inds.*, **10**, 133 (1938). The effect on milk is well described by Kasahara, Tatuini and Konisi, *Z. Kinderheilk.*, **59**, 193 (1937).

[3] Brit. 332,533 (1930).

[4] *Kolloid-Z.*, **41**, 163 (1927).

Köhler [3] extended the idea to emulsions of vegetable oils (containing free fatty acids) in dilute aqueous alkali solutions. An optimum concentration of emulsifying agent is predicted, above or below which less concentrated emulsions will form on shaking. With too little alkali, all the free fatty acid will not form soap; with too much alkali, the aqueous phase will still be alkaline when all the free fatty acid has formed soap. Experiments confirmed this prediction.

Variable quantities of olive oil were shaken with 100 c.c. of 0·02 N . Na_2CO_3 solution. The emulsion was filtered to separate undispersed oil and the turbidity of the emulsion was measured with a Kleinmann nephelometer. For quantities of olive oil (cubic centimetres) of 0·2, 0·5, 1·0, 2·5 and 5·0 respectively, the turbidities were 1·0, 1·3, 2·7, 1·7 and 1·7 respectively, thus showing a distinct maximum emulsification.

More pretentious emulsion experiments were made by Schindler,[4] who dispersed heavy mineral oil in water by the aid of sulphonated fish and castor oils. As example, maintaining constant the concentration of heavy mineral oil and varying the concentration of sulphonated fish oil, an emulsion stable for fourteen days resulted, when the oils were at their optimum concentrations (5 grm. of each for an O/W emulsion of 100 c.c.). Using less sulphonated oil gave a poor dispersion, whilst using more sulphonated oil caused coagulation. It is interesting to note that adjusting the *p*H value to the range 7·1—11·1 by addition of N . NaOH gave emulsions stable for eight days with no optimum.

Electrophoresis measurements by von Buzágh [5] with suspensions of solids in aqueous solutions of electrolytes showed that with constant quantities of the solid phase the migration velocity passed through a maximum as the concentration of electrolyte was increased. Similarly, for a constant amount of electrolyte, but variable amounts of solid phase, the migration velocity passed through a maximum. It is assumed that peptisation demands a definite electric charge of the particles and thus depends on a definite adsorption of the peptising agent. Too little solid means too large an amount of adsorbed electrolyte, whilst excess solid fails to secure enough electrolyte for its stabilisation.[6]

The application of Ostwald's rule to emulsions in general necessitates further investigation which should be carried out with emulsions of known size-frequency analyses. In place of *quantity of dispersed phase* there should be studied *interfacial area of adsorbing oil/water boundary*.

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[1] *Ibid.*, **41**, 169 (1927); **43**, 215, 220 (1927).

[2] *Ibid.*, **43**, 227 (1927).

[3] *Ibid.*, **45**, 345 (1928).

[4] *Ibid.*, **48**, 254 (1929).

[5] *Ibid.*, **48**, 33 (1929).

[6] The problem of peptisation is reviewed by Ostwald and Rödiger, *ibid.*, **49**, 314, 412 (1929). See also Auerbach, *ibid.*, **51**, 179 (1930).

Technical homogenisation processes cannot be ignored in this connection. Further, experiments should be conducted, using non-electrolytic emulsifying agents, where ionic coagulation effects will be absent; the extreme case would then be the use of solid powers as emulsifying agents.[1] That sufficient emulsifying agent is necessary for optimal dispersion of a given quantity of oil to a predetermined degree of subdivision is obviously axiomatic.

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[1] See the comprehensive account of the Bodenkörperregel in von Buzágh's "Colloid Systems" (London: 1937), p, 251 *seq.*

CHAPTER XI

THE PREPARATION OF EMULSIONS —TECHNICAL OPERATIONS

THE variety of machines intended for preparing emulsions is surprising, as a survey of the patents literature will show. From hand-worked to power-driven apparatus the range is wide. A selection of types will be discussed, the intention being to illustrate general ideas rather than to give an exhaustive account of the many types specified.[1]

The following abstracts of patent specifications demonstrate the various ideas which have been incorporated in devices for preparing emulsions. More detailed examination of the commoner principles then follow.

(1) A horizontal open-ended conduit is mounted within a mixing chamber provided with inlets for the liquids to be mixed and agitating elements are provided in the conduit and in the chamber.—(Kirschbraun, U.S. 1,603,546 (1926).)

(2) The apparatus comprises a hemicylindrical vessel with hermetically closing lid positioned as the diameter of the cylinder and with an internal paddle positioned as a radius. The paddle is provided with a number of small apertures, and when it is oscillated by an external handle, the mixture of liquids is forced through the apertures under pressure from side to side.—(McGougan and Hunter, Brit. 267,681 (1926).)

(3) At the bottom of a tank is a chamber containing a bladed rotor, the chamber being so designed that the rotor withdraws material centrally from the tank and returns it through stationary guide blades and an adjustable ring slot at the circumference of the chamber.—(Garthe, Brit. 405,503 (1933).)

(4) A body of emulsion is maintained in continuous circulation through a sinuous passage and at a point where the agitation is less intense the two phases are introduced, whilst the emulsion is removed from a point of greater agitation.—(Kirschbraun, U.S. 1,916,885 (1933).)

(5) Mixing in a deep vessel is caused by the action of a propeller in the bottom of the vessel. The propeller has two sets of blades rotating in opposite directions, the clockwise directional set being close to the sides of the tank, whilst the set with anti-clockwise motion has short blades. The effect is an intensive circulatory action.—(Poniach. Brit. 411,763 (1933).)

(6) A number of propellers are situated in superposed chambers separated by partitions having central apertures.—(Craddock, U.S. 2,008,684 (1935).)

(7) The main constituents, as in making mayonnaise, are inserted by measuring pumps into the lower part of a containing vessel carrying beaters, and additional constituents are added by similar means higher up, the finished emulsion being overflowed at the highest level.—(Chapman, U.S. 2,033,412/3 (1936).)

(8) The mixture is first agitated by beaters extending from both walls in an outer annular space and then passed through roller bearings in an inner annular space, the rotated part being preferably that common to both annuli.—(Russell, U.S. 2,115,123 (1938).)

(9) The liquid phases are measured and mixed with a gas and the mixture

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[1] See Cooper, *Trans. Inst. Chem. Engrs.*, **16**, 131 (1938); Meyer, *Farben-Chem.*, **10**, 157 (1939); Brown, *Textile Manfr.*, **61**, 383 (1935); Brothman, *Chem. Met. Eng.*, **46**, 263 (1939), gives equations for determining shear requirements in emulsification and discusses the mechanism of emulsification and the types of equipment employed.

is subjected to a high pressure and then expanded. The pressure of the mixture regulates the supply of liquids and gas.—(Fish, U.S. 1,694,589 (1928).)

(10) The phases are impelled by steam or other motive fluid through a sinuous passage, the steam preferably meeting the mixture through jets at right angles.—(Zwilgmeyer, U.S. 1,817,958 (1931).)

(11) In continuous-acting apparatus the internal phase is injected under pressure unto the mixing chamber containing the continuous phase through an atomising nozzle (situated in the base) which is in the form of an adjustable valve with an inverted conical seating. This results in the injected liquid being spread out into a flat or cone-shaped surface.—(Hoffmann, Brit. 378,066 (1931).)

(12) Two jets impinge on each other or one or more jets impinge on an obstruction.—(Lansley, Palmer and Caldwell, Brit. 470,083 (1936).)

(13) Mechanical vibrations, conveniently generated by an A.C. electromagnet, are applied to the mixed phases, the vibration-transmitting means being comprised of discs loosely mounted on a shaft.—(Wynn, U.S. 2,115,056 (1938).)

(14) The emulsion passes through slots in the wall of the axial inlet conduit, then through moving paddle rings and fixed guides alternately in a radial direction.—(Mond, Brit. 301,701 (1928).)

(15) The liquids are pumped through fine grooves formed on the surface of a plug otherwise fitting tightly in a cylinder which is separate from the pump cylinder.—(Chubb, Brit. 404,409 (1932).)

(16) A multi-stage centrifugal pump is provided with closed impeller wheels constructed of wire gauze and in wavy or zigzag formation.—(Muller, Brit. 408,468 (1933).)

(17) The apparatus comprises a centrifugal rotor with small labyrinthine passages through which the liquids pass. The outlets from the rotor are still smaller than the passages, so that the passages are maintained full of emulsion and the size of the outlets can be varied by changing grub screws or other means. A collecting casing is provided for excess feed as well as for emulsion, and in the latter are vanes for arresting the motion of the emulsion and aerating it.—(Empson, Brit. 282,466 (1926).)

(18) A wheel with flat radial paddles revolves within a casing having sharp-edged corrugations on its interior surface and provided with an inlet at the top and outlet at the bottom.—(Thordarson, U.S. 1,683,500 (1928).)

(19) A hand-operated pump has the outlet constructed by two adjacent cones or multi-start threads. The cylinder oscillates together with the supply reservoir, which is thereby agitated.—(Melmore and Fluid Pressure Pumps, Ltd., Brit. 399,014 (1932).)

(20) A dispersing plug is used with an emulsifier of the pump type.—(Fleurman, Brit. 424,732 (1934).)

(21) The ingredients are metered and separately delivered by low-pressure pumps to a mixing chamber and thence are emulsified by high-pressure pumps. The deliveries of the low-pressure pumps are controlled by by-pass valves.—(Bonfield, U.S. 1,975,631 (1934).)

(22) A long cylinder is fitted with a hand-operated plunger and has an unrestricted inlet valve at the bottom and restricted outlet at the top.—(Melmore, Brit. 431,978 (1934).)

(23) A gear-wheel pump is formed with a clearance between the casing and gears for a definite leakage, and a difference of pressure is maintained between the outlet and inlet by a spring-loaded valve to induce back-flow through the clearance.—(Bauer, Strangman and Schulman, Brit. 457,058 (1935).)

(24) A centrifugal emulsifier comprises a rapidly rotating dish which is so contoured that as the centrifugal force increases with increase of radius so also does the resistance to flow of the film of emulsion (fed to the centre). Thus, the surface of the dish rises with increasing slope outwardly, terminating, if required, with a slightly in-turned edge.—(Wait, Brit. 316,959 (1928).)

(25) The continuous phase is put into rapid rotation, as in a centrifugal pump, and the internal phase is admitted to it through a nozzle situated, *e.g.*, on the axis of the pump at the centre of the vortex formed in the first liquid. The interior of the pump casing may be provided with disintegrating pins.—(Auerbach and Steinhorst, Brit. 325,033 (1928).)

(26) A rotating bowl is provided with fixed, vertical stirrers arranged in such a way that the voids behind them are stabilised, and one liquid is dropped into the voids.—(Drucker, U.S. 1,822,275 (1931).)

(27) A high-speed impeller is co-axial with and matches the shape of a conical bottom, but those parts are eccentric with the wall of the vessel.—(Seegers, Brit. 455,891 (1936).)

(28) A number of rotating, centrifugally acting cones, on the first of which one liquid phase is spread in a thin layer ; the second cone flings the second liquid into the first.—(Edwards and Soccart, Brit. 461,772 (1936).)

Various emulsifying machines have been described by Moritz,[1] Deakers,[2] Fischer,[3] Aumarechal,[4] Andreasen, Berg and Kjaer,[5] Rajewsky and Burkhardt,[6] Cluzan,[7] and a wide variety of methods is evidenced in the following selected list of patents :—

Shropshire	U.S. 1,983,782 (1934)
Robinson	U.S. 1,958,020 (1934)
Hildebrandt-Sørenson	Dan. 48,337 (1934)
Muller	Brit. 406,468 (1934)
Reid	Brit. 415,251 (1934)
Serebrennikov	Russ. 38,624 (1934)
Hildebrandt	Ger. 590,222 (1934)
Gerrit Westerink	Ger. 621,326 (1935)
Roctor	U.S. 2,000,645/6 (1935)
Müller	Ger. 614,667 (1935)
Melmore	Brit. 431,978 (1935)
A. Jacobi A.-G.	Ger. 614,701 (1935)
Flourman	Brit. 424,732 (1935)
Craddock	U.S. 2,008,684 (1935)
Esch	U.S. 2,009,957 (1935)
Dean	Brit. 437,752 (1935)
Robinson	Brit. 438,680 (1935)
Ploberger	Austrian 143,999 (1935)
Hildebrandt	Ger. 608,702 (1935)
Schwimmer	U.S. 2,030,158 (1936)
Chapman	U.S. 2,033,412/3 (1936)
Serebrennikov	Russ. 46,535 (1936)
Alfreds	U.S. 2,026,604 (1936)
C.I.M.N.A.	Fr. 799,651 (1936)
Itterlein	Brit. 456,644 (1936)
Lansley	Brit. 470,083 (1937)
O'Neil	U.S. 2,103,549 (1937)
Fleurmann	Ger. 640,646 (1937)
Lechler	Ger. 645,546 (1937)
Marsden	U.S. 2,084,156 (1937)
Nyrop	U.S. 2,087,627 (1937)
Robinson	U.S. 2,088,926 (1937)
Wynn	U.S. 2,090,496 (1937)
Kleine	Swed. 88,221 (1937)
Edwards and Soccart	Brit. 461,772 (1936)
Hurley and Dickinson	Brit. 459,710 (1937)
Bennett (Hyde) Ltd.	Fr. 833,413 (1938)
Etzkorn	Fr. 831,781 (1938)
Navrbjerg and Rasmussen	Dan. 55,495 (1938)
Souter and Thomson	Brit. 494,204 (1938)
Ferrier, Gudel & Cie.	Swiss 195,285 (1938)
Lavine	U.S. 2,124,580 (1938)
Rank	Brit. 500,723 (1939)
Pfaudler-Werke A.G.	Ger. 675,302 (1939)
Saylor	U.S. 2,180,301 (1939)
Hawes	Brit. 501,675 (1939)
Neitzke	U.S. 2,159,670 (1939)
Olson	U.S. 2,144,994 (1939)
De Stubner	U.S. 2,148,608 (1939)
Bowen	U.S. 2,142,344 (1939)
Karsenty	Fr. 842,404 (1939)
Raves	Can. 388,177 (1940)
Hayes	U.S. 2,198,614 (1940)

STIRRING DEVICES

First, there is comparatively simple stirring mechanism such as the Hy-Speed mixer. This consists of two propellers, adjustable to varying heights on the shaft. By reversing the pitch of the lower propeller, a powerful pull up from the bottom of the mixing vessel is created, whilst the upper propeller creates a downward flow. The two opposing streams are thus forced against each other between the two propellers and then thrust against the sides of the vessel with great force. The emulsion is, therefore, in a condition of violent turbulence.

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[1] " L'appareillage pour la preparation des emulsions " (Paris, 1939).

[2] *Drum Cosmetic Ind.*, **37**, 41 (1935).

[3] *Kolloid-Z.*, **75**, 285 (1936).

[4] *Compt. rend. XVII Cong. Chim. Ind.*, **1937**, 1035.

[5] *Kolloid-Z.*, **82**, 37 (1938).

[6] *Ibid.*, **89**, 320 (1939).

[7] *Bull. trav. soc. pharm. Bordeaux*, **77**, 216 (1939).

Mixing vessels fitted with all manner of stirring devices abound in practice. A variant is the revolving cylinder, fitted with hollow trunnions carrying a horizontal revolving shaft with a number of beaters arranged to run in the opposite direction to that of the cylinder and its contents. The so-called churns employed in making margarine emulsion are large jacketed vessels with inlet pipes for oil and milk, and they are fitted with gate stirrers revolving in opposite directions. The Grasso churn of Dutch manufacture is a familiar example.

A patent granted to Duwe[1] specifies that the liquids in a tank are mixed by means of a propeller drawing upwards from the lower part of the tank and distributing the liquids in a horizontal veil over the surface. According to Hoffmann[2] a thin widely-dispersed sheet is formed of one of the liquids and the other liquid is caused to flow against this sheet. The liquids may be mixed together in a pipe by forcing at least one of them into the pipe under such pressure that its velocity is not less than that required for turbulent flow.[3] Bohm's patent describes a multiple worm agitator, whose individual worms are arranged concentrically and with different directions of pitch; the multiple worms completely fill the inner space of the emulsification vessels and cause rapid eddying movement of the contents.[4] An apparatus described by McConnaughay[5] consists of a cylindrical casing containing intercalating stationary and rotating blades. The inlets for the two liquids are spaced apart near one end and some of the blades, preferably those between the inlets, are inclined to tend to force the material back, but the majority are inclined to propel the mixture to the discharge at the other end.

The incorporation of sieves in mixing devices is an obvious suggestion, and several patents are concerned with this. According to Muller, a multi-stage centrifugal pump is provided with closed impeller wheels constructed of wire gauze and preferably in wavy or zigzag formation.[6] Hawes' apparatus comprises a cylindrical screen within which is a propeller and guide forcing the emulsion upwards and outwardly through the screen; it may be suspended at different levels, starting at the dineric interface if the two liquids are not already mixed.[7] Another patent deals with forcing under pressure (using a propeller worm) the emulsion through a series of sieves or perforations.[8] Vogelsang[9] combines injection with a cylindrical sieve.

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[1] U.S. 1,786,009 (1930).
[2] U.S. 1,926,484 (1933).
[3] South Metropolitan Gas Co., Stanier and Davis, Brit. 393·934 (1933).
[4] Brit. 28,840 (1913).
[5] U.S. 1,941,808 (1934).
[6] Brit. 408,468 (1933).
[7] Hawes, Brit. 360,171 (1930).
[8] Boothroyd Ltd. and Woolliscroft, Brit. 4623 (1909).
[9] U.S. 1,140,548 (1915).

Continuous emulsifiers with control of the volume ratio of the two phases are exemplified in the early apparatus of Blichfeldt [1] and in the well-known Silkeborg emulsifier.[2] The machine which has found somewhat extensive use in the margarine industry consists of a jacketed horizontal cylinder permitting thermal control having internal propellers with fixed sieves between. The propellers revolve at 1,600 r.p.m., a 200-gallon per hour output necessitating a 16-h.p. motor. The two liquids are fed into the cylinder continuously by adjustable pumps geared to the propeller shaft, which permit accurate and steady volume relationships.

Mixers in the process industries have been described by MacLean and Lyons [3] and propeller-type mixers by Bissell [4] who states: "True mixing requires that dispersion of the different materials end with uniform relationship throughout the mix, whether large or small samples are involved. This can be accomplished only by setting up currents within the tank in such a way that differentials in direction and velocity occur in a multiplicity of loci. It is along the margins of these streams that actual mixing takes place, as well as directly at the propeller. This phenomenon has been studied by the stria method, and new developments can be expected as a result. One fact has been well proved. The existence of swirl or vortex indicates poor mixing since there is no interchange of position between particles under such conditions. The off-centre principle of agitation does away entirely with swirl or vortex and thus secures uniformity in a shorter time than other methods. Since no baffles are required, power requirements are usually lower." The last author points out that the lack of criteria for measuring turbulence means that performance and side-by-side comparison have still to be utilised.

CENTRIFUGAL EMULSIFIERS

Many patents have been granted for apparatus involving centrifugal force. Thus, a rotating bowl is provided with fixed, vertical stirrers arranged so that the voids behind them are stabilised and one liquid is dropped into the voids.[5] Again, on the exterior of a conical plug closely fitting and rotating with a centrifugal cone a roughened passage is formed through which the liquids are forced by centrifugal force.[6]

By centrifugal action the materials of the emulsion are forced through a number of concentric rings having suitable apertures [7] or through a narrow annular passage to be subjected to impact against a wall opposed to the passage.[8] The Ferns [9] centrifugal mulsor illustrates the principle.

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[1] Brit. 4,505 (1912).

[2] Silkeborg Maskinfabrik Zeuthen and Larsen, Brit. 4,657 (1914). See also Danish 48,337 (1934); Danish 56,508 (1939).

[3] *Ind. Eng. Chem.*, **30**, 489 (1938).

[4] *Ibid.*, **30**, 493 (1938). See also Gunners and Baker, *ibid.*, **30**, 497 (1938), and the well-illustrated summary in *Food Inds.*, **9**, 109 (1937).

[5] Drucker, U.S. 1,822,275 (1931).

[6] Bendixen and Wood, Brit. 412,388 (1933).

[7] Bendixen and Vredenburg, Brit. 367,890 (1931); Serebrennikov, Russian 46,535 (1936).

[8] Norcross, U.S. 1,338,996 (1920); Leitch, U.S. 1,266,501 (1918); Williams, U.S. 1,200,559 and 1,200,560 (1916); Draper, Henry and Heninger, U.S. 1,177,236 (1916); Alexander, U.S. 994,554 (1911); Bennett (Hyde) Ltd., Fr. 833,413 (1938); Saylor, U.S. 2,180,301 (1939); Muller, Brit. 406,468 (1934); Holdsworth, Brit. 495,107 (1938).

[9] Brit. 223,347 (1924).

The apparatus consists of two or more circular metal plates or discs, which are dished or scopoed out on their juxtaposed sides in such a way that they are provided at their periphery with a sharp-edged brim. These plates are supported one above the other, brim towards brim, in such a manner that a lenticular space is left between them. This space forms an outlet for any fluids that are introduced into it, and by using, for instance, screws, rods, sleeves or the like of a certain length as distance pieces, it is possible to make the opening between the brims of any desired dimensions. The shaft carrying the plates is provided with an axial hole which is open at the top and communicates at its lower part with the lenticular space or spaces between the plates through lateral holes. The apparatus is brought into rapid centrifugal motion before the emulsion or fluids are admitted, whereupon complete mixing and fine dispersion results. In the case of milk emulsions the fat globules reach as small as 0·0001 in. diameter.

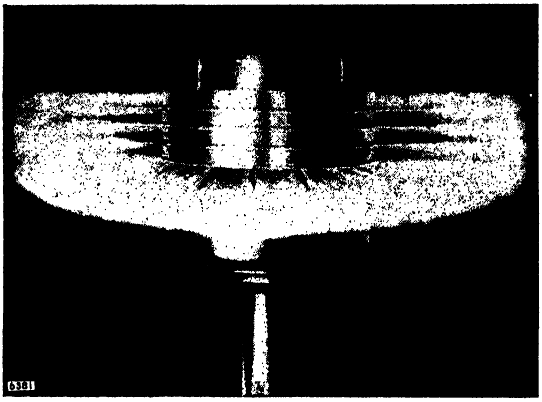

FIG. 65. De Laval emulsor.

Fig. 65 illustrates the De Laval emulsor which consists essentially of a bowl rotating upon a vertical spindle at a speed of 10,000—12,000 r.p.m. The liquids to be emulsified are roughly premixed and fed into this bowl through the regulating cover of the tinware. They first of all pass through a small clarifying space in the bottom of the bowl to remove foreign particles. The liquor then passes upwards and is thrown out by centrifugal force through a number of very fine slots. In the case of a liquid of low viscosity such as reconstituted milk or ice cream, these slots are 0·002 in. wide, and in the case of more viscous systems their width is increased to 0·005 in. The shearing action on the liquid during its rapid passage through these fine slots causes emulsification, which is further enhanced when the spraying liquid hits the collecting covers of the machine.

Two sizes of emulsors are made : No. 1 with a capacity of 110—220 gallons per hour has a power consumption of 1·5 to 2 h.p., while the No. 2 has a capacity of 44—88 gallons per hour with a power consumption of 0·3 to 0·5 h.p. The output is, of course, a function of the viscosity of the system treated.

PRE-ATOMISING DEVICES

Instead of smashing both liquids constituting an emulsion, the idea of atomising the internal phase has been given considerable attention. In this connection reference is made to an interesting investigation by Halberstadt and Prausnitz,[1] who measured the size of globules of a liquid forced into a second immiscible liquid through perforations in metal sheets. The diameters of the globules decreased as the pores were smaller ; interfacial tension, of course, also influenced the size. The idea is embodied in a patent granted to Bendixen,[1] who claims that the emulsion is forced through pores in a partition at an angle to the main stream.

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[1] *Z. angew. Chem.*, **43**, 970 (1930).

According to a patent by Gropengiesser,[2] in making margarine (O/W) emulsion, the atomised liquid fats of globule-size, 0·001—0·0001 mm. diameter, are introduced under the surface of violently agitated milk containing egg yolk. Several patents relate to injection methods for preparing artificial cream [3] or lubricants.[4] De Cew [5] states that the oil to be emulsified and water are separately heated and forced by impact against each other from atomising orifices under super-atmospheric pressure to produce an emulsion, which is then discharged into cold water.

Recalling Sumner's condensation method, the patent granted to Agthe [6] is of special interest. The oil is atomised with steam in the form of a hollow fluid jet with the interior and exterior of which the material treated is caused to come into contact ; the atomised material is incorporated in a dispersion medium such as an aqueous solution in which the atomising agent condenses and within which the atomisation is effected. An electrical method for introducing the disperse phase in a finely-divided condition into the external phase is described by Auerbach.[7]

Closely-related methods employ air or steam to effect emulsification. Heitmann [8] passes gas into oil to break this up ; water is added and the gas stream is continued to effect mixing. Emulsification inside a steam injector, aided by the condensation of the steam, is claimed by Erfurt.[9] Zwilgmeyer [10] claims to mix the two phases and then impel them through a sinuous passage, the steam meeting the mixture through jets at right-angles, as in a scent spray. The liquids may be forced tangentially into a chamber, whence they issue axially as a spray.[11] Another patent claims that the phases are sprayed through at least two nozzles so as to impinge on each other or on a common surface ; at least one of the nozzles is multiple so that a motive fluid such as steam or compressed air may be used, and partly-mixed materials are lifted back into the spray. Thus, linseed oil may be sprayed by steam and ammonium oleate solution is simultaneously sprayed by compressed air.[12]

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[1] Ger. 466,353 (1925).

[2] U.S. 1,958,820 (1934).

[3] Benzon and Jensen, Brit. 362,744 (1931) ; Bergsvik and Vitacream Ltd., Brit. 335,159 (1930) and 334,863 (1930) ; Gould, U.S. 1,400,484 (1921).

[4] Fitts, Brit. 397,317 (1933) ; De Cew, U.S. 1,317,617 (1919).

[5] U.S. 1,330,174 (1920).

[6] Brit. 210,307 (1923) ; U.S. 1,668,136 (1928).

[7] Ger. 521,644 (1929) ; *Kolloid-Z.*, **74**, 135 ; 285 (1936).

[8] U.S. 1,724,653 (1929).

[9] Brit. 24,375 (1907).

[10] U.S. 1,817,958 (1931).

[11] Lechler, Brit. 362,430 (1930).

[12] I.C.I. Ltd., and Clarke, Brit. 331,928 (1929).

The influence of imposed electrostatic charge on liquid streams has been described by Auerbach[1] who suggests that highly charged W/O emulsions may be used as "liquid accumulators," the emulsions being transportable and the electricity recovered at will.

COLLOID MILLS

Mechanical dispersions to colloid dimensions received considerable impetus through the advent of the so-called colloid mills.[2] Much interest was shown in the early Plauson mill,[3] although its operation on the batch principle and its heavy power consumption brought about a subsequent decline in popularity.

A hammer mill has the disadvantages that an increase in speed increases the air resistance and much heat is evolved uselessly. Again, the finest particles, still awaiting further dispersion, escape the beaters and are carried through the gratings with the air stream. A ball mill has the disadvantages that the velocity of fall of the balls is small, the work done per blow small and the number of blows few. Such considerations led Plauson to modify a hammer mill so that the beater arms impinged on a *liquid* surface. Further, he operated the rotor at very high peripheral speed to increase the number of blows in a given time.

A detailed description of the mill and of the theory involved has been given by Block.[4] The mill consists of a water-cooled cylindrical casing with axis horizontal, and an eccentrically mounted rotor whose projections work past similar projections fixed on the casing and on an adjustable bottom bed-plate. When the rotor is run at a high speed the liquid is flung off the rotor and again sucked in, bringing fresh particles into contact. The centrifugal force also sets up a rotation of the liquid in the casing. The mixture to be dispersed enters at the top of the machine and is discharged at the bottom of one side.

Later, Plauson has described a colloid mill with intermeshing gears, between which the material passes for grinding.[5]

A variety of colloid mills exists and several detailed accounts of the various types have been published.[6] The present treatment will be confined to the more common mills in actual factory use.

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[1] *Kolloid-Z.*, **43**, 114 (1927).

[2] *Vide* the interesting paper by Podszus, *Kolloid-Z.*, **64**, 129 (1933) on the theory of mechanical dispersion to colloid dimensions.

[3] *Chem. Ztg.*, **44**, 535, 565 (1920); *Engineering*, **90**, 429 (1920); *Z. angew. Chem.*, **34**, 469 (1921); Ditmar, *Farven-Ztg.*, **27**, 433 (1921); *Chem. Ztg.*, **45**, 943 (1921); Forster and Reilly, *J. Soc. Chem. Ind.*, **41**, Review, p. 435 (1922).

[4] *Z. angew. Chem.*, **34**, 25 (1921); *Wiss. u. Ind.*, **2**, 71 (1923); *Farben-Ztg.*, **32**, 459 (1926). See also Kenney, *Chem. Met. Eng.*, **27**, 1080 (1922); Schotz, *Chem. Age* (*London*), **6**, 790 (1922); **14**, 99 (1926); Ginsberg, *Oil, Paint Drug Rep.*, **100**, (i), 24, 84 (1921); Naske, *Z. Ver. deut. Ing.*, **65**, 495 (1921).

[5] U.S. 1,923,013 (1933); Brit. 324,977 (1928); Ger. 664,915 (1938); Auspitzer, *Ind. Eng. Chem.*, **20**, 413 (1928), describes the Oderberg colloid mill, an improved type of the Plauson mill, requiring only 1/7 of the power. See also Auspitzer, U.S. 1,577,052 (1926).

[6] Chwala, *Kolloid-Z.*, **55**, 122, 371 (1931); **56**, 117 (1931); Podszus, *ibid.*, **56**, 122 (1931); Frydlender, *Rev. prod. chim.*, **31**, 81, 121 (1928); Naske, *Chem. App.* ,**17**, 157, 195 (1930); Hebber, *Chem. Fabrik.*, **1928**, 581; Grohn, *ibid.*, **1931, 1**, 13, 27; Travis, *Ind. Eng. Chem.*, **21**, 421 (1929).

THE "PREMIER" COLLOID MILL

Fig. 66 refers to a section of a 5-inch horizontal type mill[1] which has working parts consisting chiefly of a rotor and a spindle RS and a starter S, the working surfaces being at WS. The rotor consists of a perfectly smooth face upon the frustrum of a cone. The surface of the stator S is an-integral part of the removable casing, and is also ground to very fine limits. The arrangement and adjustable relation of the rotor RS and the stator S is suggestive of the clutch in a motor car, except, while in operation, the aperture or clearance is fixed and the surfaces are never in actual contact. The clearance is always fine and varies from $\frac{2}{1000}$th of an inch upward according to the materials and the desired degree of dispersion.

The spindle is mounted in ball bearings " B.B.," which are themselves housed in a cylinder CY, which cylinder is a piston fit in the casting PC. The cylinder CY may be locked in the casting PC by means of the locking device LD. The adjustment of distances between the stator and the rotor is made by slacking off the locking device LD and adjusting the clearance by means of the ring AR. The mill is driven by means of a very thin rubber belt on the pulley P. The normal speed of this mill is approximately 9,000 r.p.m. The material to be treated is fed in through the inlet IN, passes through to the working space WS and leaves by the volute VO.

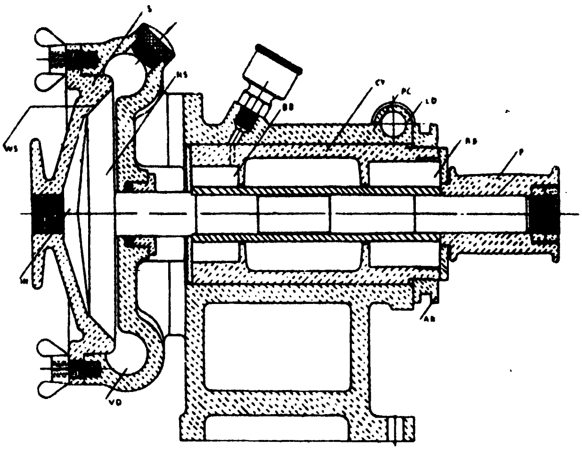

FIG. 66. Premier high-speed mill—horizontal type.

The dispersion occurs within the liquid medium or film while passing between the rotor and stator. The degree of dispersion is dependent upon two factors, the clearance and speed ; the smaller the clearance and higher the speed the greater the disruptive force and consequent dispersion.

A vertical type of mill, the so-called paste mill, has working parts similar in principle. It is, however, directly driven from a vertical motor through a coupling. It has a very large run-off which, in special cases, may be duplicated, one on either side of the mill. Again, the working head is jacketed for thermal control.

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[1] See Ross, *Chem. Met. Eng.*, **37**, 425 (1930) ; Claflin, *Leather Manufr.*, **42**, 59 (1931) ; McClean, *Refiner and Nat. Gasoline Manufr.*, **3** (viii), 29 (1924) ; *Ind. Eng. Chem.*, **16**, 494 (1924) ; *Can. Chem. Met.*, **8**, 284 (1924) ; China, *Proc. Chem. Eng. Grp.*, V—VI., A. (1923—4), 126 ; Burt, Boulton and Haywood Ltd., and China, Brit. 221,442 and 221,548 (1923) ; China, *Ind. Chemist*, XI., 15 ; 103 (1935) ; Fr. 782,025 (1935).

Range of Horizontal High-Speed Mills

Rotor Diameter.	Normal Running Speed.	Usual Method of Drive.	Usual Motor Supplied.	Approximate Hourly Output.
3½ in. .	15,000 r.p.m.	Flat belt.	2 h.p. at 3,000 r.p.m.	15/20 gals.
5 in. .	9,000 r.p.m.	Flat belt.	3 h.p. at 3,000 r.p.m.	40/60 gals.
10 in. .	4,500 r.p.m.	Texrope.	10/15 h.p. at 1,500 r.p.m.	300/450 gals.
15 in. .	3,000 r.p.m.	Texrope or Direct-coupled to motor.	25/30 h.p. at 1,500 r.p.m. or 25/30 h.p. at 3,000 r.p.m.	1,200/1,500 gals.

Range of Vertical Paste Mills

Rotor Diameter.	Normal Running Speed.	Usual Method of Drive.	Usual Motor Supplied.	Approximate Hourly Output.
2½ in.	3,000 r.p.m.	Direct.	½ h.p.	40/60 lbs.
5 in. .	3,000 r.p.m.	Direct or belt.	6 h.p.	4/6 cwt.
10 in. .	3,000 r.p.m.	Direct or belt.	15/20 h.p.	12/20 cwt.

It must be noted that the approximate hourly outputs given above are meant to serve only as an indication. The output depends upon both the viscosity of the material under treatment and the clearance between the working surfaces.

THE "PREMIER" CORRUGATED MILL

A new type of colloid mill has been evolved.[1] Referring to Fig. 67, it will be noticed that the working surfaces—namely, the rotor RS and the stator cover C—are no longer of simple form. The co-operating faces of the stator and the rotor are provided with V-shaped corrugations, the angles of which are so designed that the cross-sectional area of the space

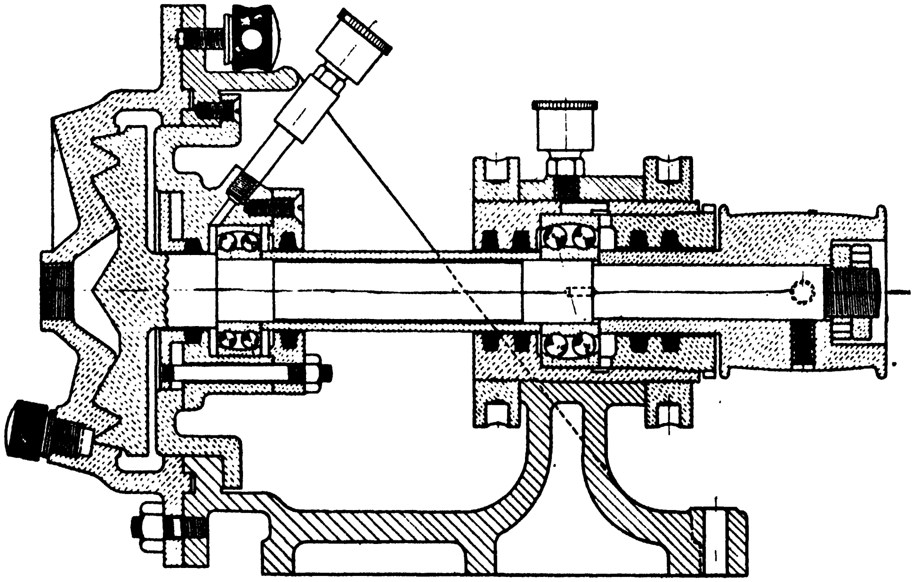

FIG. 67. Premier corrugated colloid mill.

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[1] China and Premier Colloid Mills Ltd., Brit. 432,570 (1934).

between the grinding members at the periphery where the material is discharged can be made equal to or less than the cross-sectional area of the space at the centre, namely, the point at which the material is supplied. In this manner, under working conditions, the space between the grinding members can be kept not only full of material but automatically kept also under pressure. Again, with such an arrangement of the angles of the corrugations, while all surfaces are touching when the rotor and stator are put together, the clearance is not the same for all the corrugations when the rotor and stator are opened slightly; the clearance between them is automatically made decreasing as one passes outwards to the periphery.

It is claimed that emulsification is progressive; the time during which disruption takes place is increased, giving longer time for adsorption of the emulsifying agent. Provided that the filling funnel is kept full, air cannot be entrained in the working film. The outlet from the mill is in the cover, which is supplied with a suitable cock, which enables the output to be restrained in order to keep the whole process under any pressure desired up to 30 lb. per square inch. Mills are made up to a size giving an output of 1,800 gallons per hour.

BARTLETT-SNOW COLLOID MILL

The new colloid mill (Fig. 68) with triple processing action, introduced by The C. O. Bartlett and Snow Co., Cleveland, Ohio, is of the vertical type. Material is fed downward through a receiving funnel, A, and encounters the impeller vanes, B, on top of the rotor travelling at 10,800 r.p.m., which force it to the periphery of the rotor at pressures as high as 150 lb. per square inch for some materials. The material is sheared at C in passing downward between the side of the rotor and the housing (first processing action), is then impelled against centrifugal force by the pressure of oncoming material through a labyrinth of tight-fitting circular rings, D, machined on the bottom of the rotor and the top of the stator (second processing action), and then forced across the smooth section, E, between the rotor and the stator (third processing action) and drains from chamber F through the side discharge outlet without having come in contact with any packing or glands at any time.

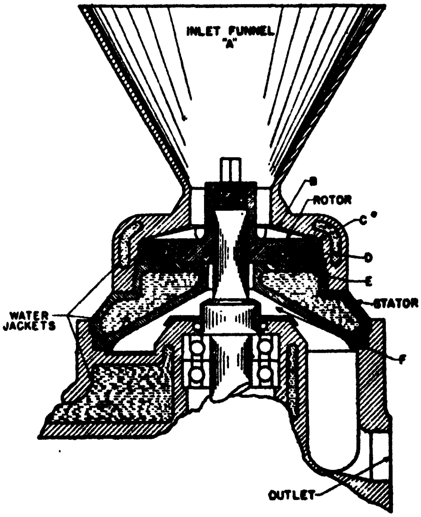

Fig. 68. The Bartlett-Snow colloid mill.

THE "HURRELL" COLLOID MILL

The short cylindrical body of the machine [1] is provided with a complete annular jacket for steam heating or water cooling. The bore of this member constitutes the stationary working surface. Two circular covers are bolted to the stator; these are equipped with glands through which the rotor shaft passes, and upon extended arms cast with the covers are housed the ball bearings. One of these bearings is carried within a bronze sleeve which slides in the bracket arm; this sleeve is in screw engagement with a large hand-wheel, by rotating which the "gap" or film thickness is adjusted, and this adjustment is particularly bold and simple—each half turn of the hand-wheel modifies the gap 0·001 in. The rotor, which is carried upon a heavy alloy steel-hardened shaft, is of massive construction; the periphery is almost, but not quite, parallel, and the slight taper (similar to the bore of the rotor) enables the adjustment mentioned above to be made.

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[1] Hurrell, Brit. 245,929 (1925) and 389,095 (1931); U.S. 1,756,198 (1930).

The materials (liquids or liquids with solids in suspension) are fed into the hopper either from overhead tanks or by pumps. From the hopper they pass vertically to an enlargement near the centre, whence they flow into the annular space between the two halves of the rotor. Being confined within this space, they are flung to the periphery by centrifugal force and thus create the pressure necessary to force them through the fine gap between the rim of the rotor and the bore of the stator. The automatic control of rate of through-put is secured by this construction.

By reason of the practically parallel cylindrical form of the rotor, there is no tendency on the part of the fluid in the gap to leave the space due to its own inertia; the displacement is effected by a ring of liquid of varying radial depth in the annular space. If the materials are fed so slowly that there is practically no radial accumulation, many revolutions will take place while the contents of the gap traverse the working face, and they will receive consequently a vastly greater thoroughness of treatment than that effected at the maximum rate of feed. This maximum is arrived at by delivering the materials to the feed tube at such a rate that the annular space is kept entirely filled with liquid. Any intermediate rate is secured by regulating the supply to a suitable degree; thus a wide range of intensity of treatment (in practice from 10 to 1,000 gallons per hour on a No. 1 machine) is effected without any alteration or adjustment of the machine. The location of the impelling space in the mid-length of the working gap has another very important advantage, viz., the fluid thrust between the fixed and revolving part of the machine is absorbed without imparting any stress to the bearings, which have practically no work to do beyond resisting the pull of the belt.

The discharge of the finished product takes place from two outlets, one situated at the bottom of each of the covers.

The various sized mills are rated as follows :—

Size.	Output.	H.P. Motor.
	gall./hr.	
L	5—20	2
00	40—100	7·5
1	400—600	30

Sibree[1] employed a Hurrell colloid mill in certain of his experiments on emulsions. Emulsifying viscous paraffin oil in 1 per cent. aqueous sodium oleate by the aid of a Hurrell mill, he observed that 80 per cent. of the oil globules were below 4μ in diameter.

Fig. 69 illustrates the latest "C" model, an air-free pressure delivery mill, especially designed for avoiding frothing or even occasional air bubbles in emulsions, and enabling delivery against an appreciable head for elevation to storage tanks.

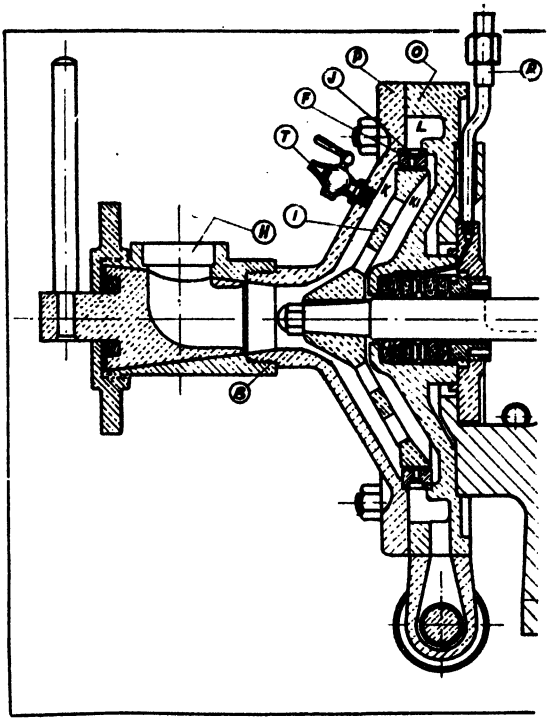

FIG. 69. Section through Type C Hurrell colloid mill.

It will be noted that the rotor somewhat resembles the impeller of a centrifugal pump without the vanes. The crude emulsion or the two phases in separate streams enter through the bore H and are carried round by the rotor I (the latter being pierced with holes so that the fluid pressure is balanced) within the space K,KI. At the periphery there is a considerable static head created which forces the liquids from both sides across the face of the stator

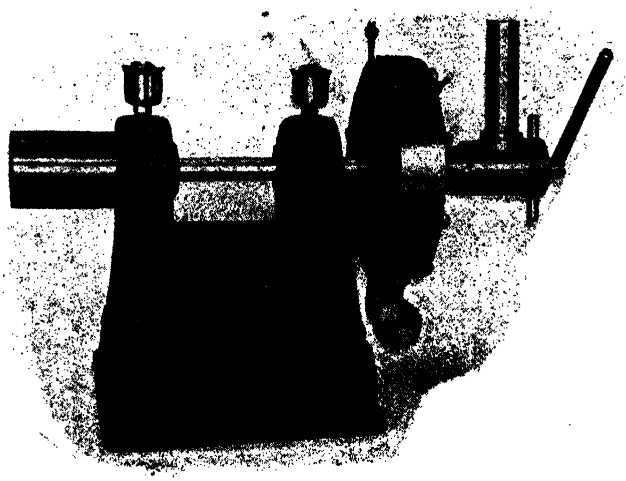
FIG. 70. Type C6 Hurrell colloid mill.

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[1] *Trans. Faraday Soc.*, **27**, 173 (1931).

ring F. Arriving at the mid-length of this stator ring fully emulsified, they enter the groove formed in the mid-length of the ring, and pass, *via* the holes J, to the receiving space L; thence they are allowed to pass out of the mill through a needle valve which can be set to regulate through-put to any desired amount. Special means are taken to prevent entrainment of air; these consist in equipping the stuffing-box with a perforated metal ring to which liquid forming one of the phases of the emulsion, either the oil or the aqueous solution, is fed at a slight pressure so that should the gland packing not be perfectly tight, liquid will be carried through into the machine instead of air.

Type " C " mills are made in two sizes, C.6 and C.4, the latter being the small-scale apparatus. The latter has an output of between 10 and 20 gallons per hour, the former (Fig. 70) between 40 and 80 gallons per hour. The speed of the C.4 is generally between 8,000 and 10,000 r.p.m., and that of the C.6 between 4,500 and 6,000 r.p.m. At these speeds the horse-power consumed may be taken as 2—3 for the C.4 and 5—10 for the C.6, the lower horse-power figure representing the consumption at the lower speed.

THE U.S. COLLOID MILL

This mill, developed by the U.S. Colloid Mill Corporation of New York, uses two flat grinding discs facing each other and revolving in opposite directions. By mounting removable grinding rings on these rotors it is possible to increase the surface area of these rings (Fig. 71) to any desired extent by merely using wider rings.

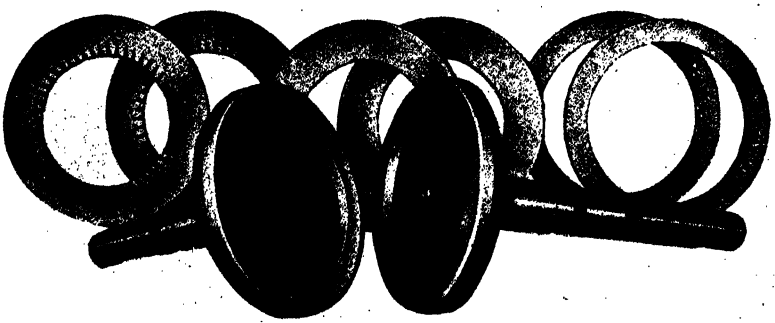

FIG. 71. Grinding rings for mounting on the rotors of the U.S. colloid mill.

Great shearing action is exerted on material which is passed between the rotors, whose distance apart is controlled from 0·001 to 0·05 inch. The material to be treated is fed to the mill by means of a small pressure pump. The mill is so designed that it may be fed either from the periphery of the rotor and discharged from the centre, or fed from the centre of the rotor and discharged at the periphery, but in either method the mill itself does not exert any suction. The adjustment for the various widths of grinding gap consists of an adjusting ring, which when rotated either increases or diminishes the width of the gap. This ring is graduated and the adjustment is locked by a pin which passes through the ring into the body of the mill.

Being surrounded by a water jacket, heating or cooling of the medium is controllable. The grinding rings are provided with radial teeth through which the material being treated passes before entering the colloidal or smooth part of the ring. These teeth, having one face at right angles to the rotor face, and tapering from about a ¼-inch opening at the intake side to zero at the colloidal gap side of the ring, exert a scissor-like shearing action and reduce the coarse particles to a relatively fine degree before they pass into the colloidal gap. The rotors range from 8 inches diameter in the intermediate horizontal type to 13 inches diameter in No. 2 horizontal type; two motors are necessary, 5 h.p. and 10 h.p. respectively, for the mills mentioned, the respective rotations being 3,600 and 1,750 r.p.m.

THE CHARLOTTE COLLOID MILL

This mill, built by the Chemicolloid Laboratories Inc., of New York, is illustrated in Fig. 72. This high-speed mill consists essentially of a *grooved* conical rotor which rotates within a correspondingly *grooved* conical stator, the clearance between them being regulated by a calibrated adjustment device. The materials to be dispersed are fed into the inlet of the mill by gravity and are forced into the gap between the rotor and stator by centrifugal force.

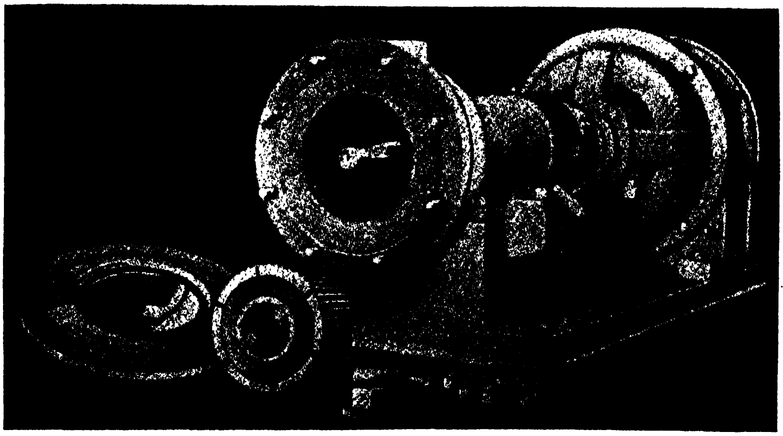

FIG. 72. The Charlotte colloid mill with cover and rotor removed.

While smooth surface mills depend for their action on the hydraulic

Type.	Horse-power required.	Capacity Gallons per Hour.	Total Grinding Surface. Sq. in.	Speed R.P.M.
650	20	100—200	143·0	3,600
725	30	200—400	159·5	3,600
800	40	300—600	176·0	3,600
850	50	400—1,000	192·5	3,600
1,050	75	1,000—3,000	231·0	3,600

shear set up between a dynamic and static element, the grooved rotor and stator of the Charlotte mill set up within these grooves whirling currents of the materials; due to this eddy action, the materials are subjected to a great beating and chopping action,. Thus, the mill employs both hydraulic shear and impact action.

Specifications of the mills are given in Table on p. 385.

THE HATT-DUSSEK "HOMOGENISER"

This is a colloid mill [1] developed in the first instance for the preparation of bituminous emulsions. It comprises a stator in the form of a casing in two halves, A, and a rotor formed in two parts, B, keyed to the driving shaft C (see Fig. 73).

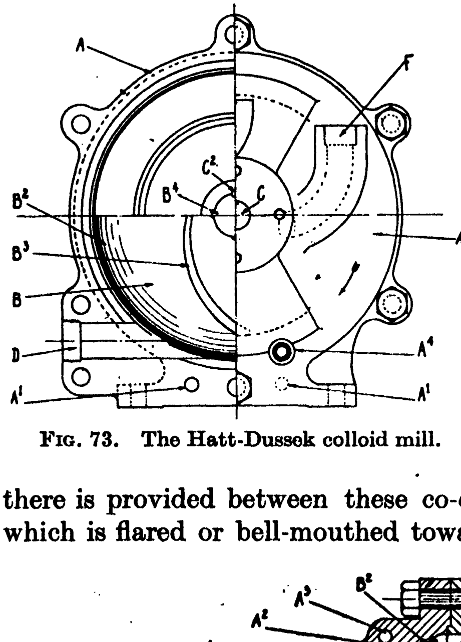

FIG. 73. The Hatt-Dussek colloid mill.

The two halves, A, of the casing are adapted to interengage when secured together by circumferentially-spaced bolts as shown in Figs. 74 and 75, dowel pins A^1 being provided to ensure accurate registration of the two halves during assembly. The inner surface, A^2, of the casing and the adjacent co-operating outer surfaces, B^2, of the rotor are parabolically curved, the centres of curvature being so arranged that there is provided between these co-operating surfaces a clearance space which is flared or bell-mouthed towards the inner end and decreases in width towards the outer end. Each of the two halves of the casing has an internal conduit, A^3, for steam, hot water or other thermal medium introduced at A^4 and discharged at A^5, or *vice versâ*.

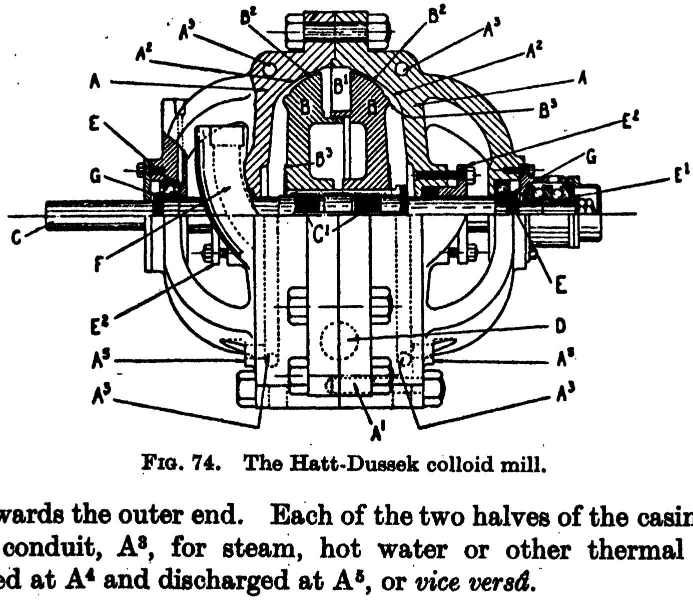

FIG. 74. The Hatt-Dussek colloid mill.

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[1] Brit. 368,719 (1932).

The two parts, B, of the rotor engage in an axially slidable manner and provide between them an annular space, B^1, with which communicates a discharge pipe, D, tangentially arranged in the casing. The rotor parts are provided with vanes or ribs, B^3, and are internally threaded to engage respectively left- and right-handed threads, C^1, on the shaft. C, keys, C^2, engaging key-ways, B^4, in the rotor parts, B, and similar key-ways, C^3, in the shaft, C. The keys, C^2, are locked in position by a locking ring, C^4, which is in turn locked to the shaft, C, by a stud, C^5.

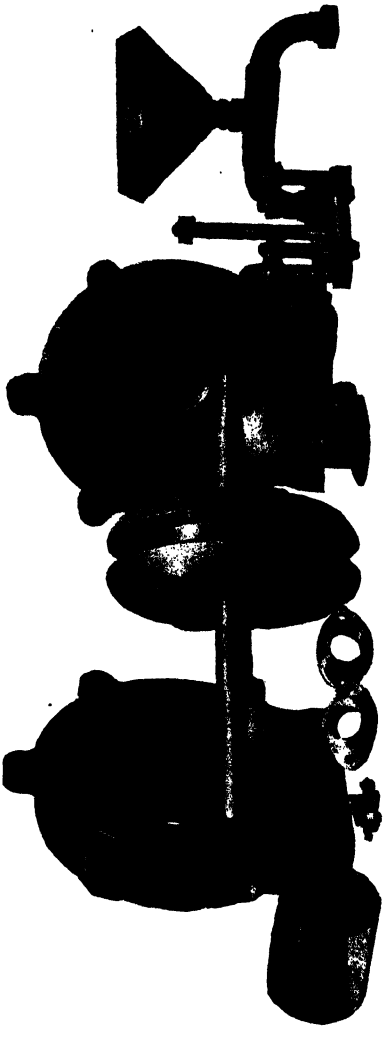
FIG. 75. Assembly of parts of the Hatt-Dussek colloid mill.

The rotor parts, B, are so designed that they are slidable on the shaft, C, independent of the threads, C^1. This ensures that the rotor is concentric with the casing. The shaft, C, is journalled at each end in a bearing E, held in position by the locking ring, G, and at one end in a double thrust bearing, E^1, by which the initial setting of the rotor, B, symmetrically within the casing, A, is effected, this bearing also serving to take up any end thrust which may take place when the machine is running.

When the shaft, C, is rotated and the liquids to be emulsified are fed under a predetermined head through the pipes, F, the liquids are thrown radially outwards by the vanes, B^3, and are thus rapidly and evenly blended prior to their entering the clearance spacings. Thus the liquids are assisted in their passage through the clearance spaces by centrifugal force and pass through each of the clearance spaces in the form of a spreading film, the thickness of which gradually decreases until the thoroughly emulsified system enters the annular passage, B^1, and is discharged through the pipe D.

Three sizes of the mill are available, thus :—

Size.	Output (galls./hr.).	R.P.M. Rotor.	Power Consumption.
1	5,000	1,300—2,000	5—7 h.p.
2	1,500	2,000—3,000	2—2½ h.p.
3	500	3,000—4,000	½—1 h.p.

According to a later patent granted to Hatt and Simms,[1] an apparatus of the shearing type is arranged so that although the thickness of the clearance space decreases in the direction of travel, its cross-sectional area remains approximately constant. This may be effected by forming both the rotor and the casing (preferably twinned) with a parabolic contour, adjustments being effected by separating the two discs of the rotor as required.

The great interest displayed in the patent literature in regard to colloid mills is reflected in the following selection from specifications :—

(1) A disc is mounted upon a shaft and adapted to rotate inside a fixed disc-shaped casing, to the centre of which one phase of the emulsion is supplied so as to pass from the centre to the circumference of the mill. The other phase (usually the oil) may enter through a tube extending transversely across the casing and communicating with the interior of the casing through various small passages at different distances from the axis. The disc may be made with a number of slots or channels, preferably of concentric circular segmental form, so as to afford free communication between the two sides of the disc, so as to equalise pressure.—(Blichfeldt, Brit. 18,048 (1914). See also Brit. 7,498 and 7,499 (1912).)

(2) The emulsion is driven through a circular slot which is formed on the one hand by an annular surface of a stationary grinding member, and on the other by a continuously rotating friction disc pressed against the said annular surface.—(Altonaer Margarine-Werke Mohr G.m.b.H., Brit. 1,227 (1919).)

(3) The emulsifier consists of two discs having on their adjacent surfaces a series of concentric circular grooves, the grooves of one disc being eccentric to those of the other.—(Davis, U.S. 1,269,399 (1918).)

(4) The mill is characterised by the combination of a conical casing, a stationary frame on which this is mounted, a conical rotor (this being the working surface) rotatably mounted within the casing. Both of the co-acting surfaces are divided into a series of working surfaces by oppositely disposed annular grooves.—(Christensen, Brit. 129,757 (1919).)

(5) The liquids traverse small circuitous passages formed between a rapidly-rotating disc and a plate affixed to same. (Andersen-Orris, Brit. 284,910 (1927).)

(6) Grinding takes place between a fixed stone with a conical space hollowed out on its underface and a lower cone rotated by a vertical shaft.—(Baier and Hammer, Brit., 290,374 (1927).)

(7) The mill comprises two relatively rotatable grinding elements within a casing. The inlet for material is to the outside of the grinding elements, and outlet for emulsion from the space between the grinding elements through the hollow shaft of one of them. The casing may be split in the same plane as the operating surface between the two rotating elements—(Eppenbach, Brit. 306,502 (1927) ; U.S. 1,728,178 (1929).)

(8) Two discs rotate closely to each other at high speed ; each disc has a groove on its working face. Fixed curved guides and collecting channels are arranged so that there is a gradual deflection and reduction of speed of the outflowing emulsion.—(Surtees, Brit. 266,098 (1926) ; cf. Andersen, Brit. 312,351 (1929).)

(9) The mill consists of a conical and fluted rotor, the stationary cone being similarly fluted. The liquids are fed to the smaller end of the rotor. A helical rotating blade assists such feed by centrifugal force.—(Ostermann, U.S. 1,885,283 (1932).)

(10) Film-shearing surfaces are used which approximate a portion of the Schiele curve in radial sectional contour.—(Tolman, U.S. 1,927,620 (1933).)

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[1] Brit. 414,689 (1934).

(11) Comprises rings of pins or triangular ridges alternately on oppositely rotating discs.—(Ross, U.S. 1,937,788 (1933).)

(12) A pair of flat discs, one of which is rotated at high speed, are provided with concentric rings of teeth, of triangular cross-section, which intercalate with each other. Each disc is provided with a number of slots or grooves running from the centre to the periphery, the slots being inclined to radii and in opposite directions on opposed discs. The clearance between the discs is adjustable over the range 0·0001 and 0·03 inch.—(J. Harrison Carter Ltd., May and Barradell, Brit. 214,521 (1923).)

(13) A colloid mill consisting of a pair of discs, preferably with concentric, intercalating corrugations, rotating at high speed in opposite directions, is provided with a main feed of material at the centre of the discs, also with an auxiliary feed to a zone between the centre and circumference, the passages for this being formed in the thickness of one disc. The portion of the discs between the centre and the auxiliary inlets may be provided with teeth (interrupted corrugations) to provide a preliminary grinding action upon the material entering by the main feed.—(Rissik, Fraser & Co. Ltd., and Fraser, Brit. 243,052 (1924).)

(14) Two discs rotating in opposite directions have intercalating ridges, thus forming a sinuous passage. The inlet to the mill is axial and outlet is peripheral, but one disc has a deep flange embracing the other disc and this causes the final outlet to be comparatively close to the axis.—(Cunniff, U.S. 1,666,640 (1926).)

(15) The emulsifying chamber comprises one fixed and one rotating wall, on each of which there are annular projections forming recesses which are inclined in opposite directions on opposite walls.—(Butler, U.S. 1,624,037 (1927).)

(16) The mill comprises two horizontal discs rotating co-axially in opposite directions at high speed. The material is fed through the centre of the upper disc to the space between the discs, and leaves at the periphery. The working faces of the discs are provided with intercalating annular teeth of buttress form, the steep faces being towards the axis.—(T. Broadbent & Sons, Ltd., and Hallitt, Brit. 308,095 (1928).)

(17) The liquids are passed through ball bearings, the inner races of which are rotated by a casing and disc fixed on a vertical shaft, while the outer races fit closely against the inner walls of the housing and are adapted to be forced towards each other in a vertical direction by a diaphragm and adjustable spring. The spaces between the casing and disc are filled by intermedate pieces.—(Siemens u. Halske A.-G., Brit. 235,227 (1925).)

(18) The cylindrical or slightly conical co-operating surfaces are provided with axial grooves of which the width of the teeth is less than that of the channels. The action has three elements : film-shearing when the teeth are opposite each other, film-beating when the teeth are approaching, and churning when the grooves are opposite.—Dawson, U.S. 1,807,773 (1931).)

(19) A colloid mill is contained in a casing, and the material is supplied under positive pressure and withdrawn under negative pressure by means of a pair of gear-wheel pumps operated by a common motor. Two containers are used, filled and emptied alternately by the same material until it is sufficiently dispersed, but the material always flows through the mill in the same direction, the change-over of flows being effected by a rotary valve.—(Dixon, U.S. 1,702,380 (1929).)

(20) A centrifugal type mill consists of a multi-stage high-pressure pump, provided with a comminuting resistance, the edges of which are smooth, stepped, or undulating against the direction of flow of the emulsion, and with perforated blades perpendicular to the direction of flow. The angle of the centrifugal blades is larger than that necessary for obtaining the maximum suction, so as to obtain a maximum beating action.—(Maschinenbau-Anstalt Humboldt, Ger. 413,143 (1923).)

(21) Supply the liquids through a hollow shaft to the space between duplicate rotor elements on the shaft. Each element is provided with a set of emulsifying surfaces arranged at an angle to each other ; each set co-operates with a corresponding set of simliar surfaces on an outer stator member to provide emulsifying clearances.—(Molin, U.S. 1,650,088 (1927).)

(22) The mill comprises a fluid-tight casing in which a beater rotates at high speed with large clearances and is preferably eccentric to the casing. The beater may be constructed of a number of thin sheets of metal with fine teeth, or of a number of layers of wire gauze from the edge of which wire strands project, or of alternate layers of each.—(Whatmough, Brit. 304,178 (1927).)

(23) A chamber contains two interacting toothed rollers which serve as emulsifiers and to the chamber a pipe connects the feed hopper. The discharge pipe from the chamber is provided with an auxiliary branch by means of which the emulsion may be returned to the chamber for re-treatment.—(McGougan and Hunter, U.S. 1,671,868 (1928).)

(24) A disintegrator of the intercalating-pin type.—(S.O.S. Patents Co. Ltd., and Reddrop, Brit. 441,215 (1934).)

(25) In a cylindrical casing containing intercalating stationary and rotating blades, the inlets for the two materials are spaced apart near one end and some of the blades, preferably those between the inlets, are inclined to tend to force the material back, but the majority are inclined to propel the mixture to the discharge at the other end.—(McConnaughay, U.S. 1,941,808 (1934).)

(26) Pins project from relatively rotating discs, the pins being drilled tangentially to the circles they describe. The relatively moving rings of pins are closely spaced in pairs with considerable free space between the pins.—(Esch. U.S. 2,009,957 (1935).)

(27) A disk mill comprises a revolvable disk and stationary disk provided with intercalating pegs of truncated pyramidal form, the clearance between the ends of the pegs and the opposing disk decreasing from the centre toward the periphery and the disks being concave with flat peripheral surfaces.—(Van Gelder, Brit. 455,666 (1936).)

(28) The apparatus comprises one or more sets of interengaging toothed wheels that are separately driven by shafts, there being considerable interplay between the teeth of each wheel, which do not come into contact with each other.—(Gerber, Brit. 503,315 (1939) and Ger. 677,646 (1939).)

(29) The materials are passed through small circuitous passages formed between a rapidly-rotating disc and a plate screwed thereto.—(Andersen-Orris, Brit. 284,910 (1927).)

(30) A rotor with vertical axis comprises spokes driving upper and lower annular discs with concentric corrugations and runs with fine clearances between upper and lower fixed annuli, which are maintained the correct distance apart by a sleeve of stiff gauze or perforated metal. The whole is submerged in a container for the material which enters the centre of the rotor from above and below, passes through the sinuous spaces between the discs, and leaves through the gauze. Excessive whirlpool action is prevented by scoops and returning the emulsion to the centre.—(Snow, Brit. 305,711 (1927).)

(31) A rotating member provided with blades, teeth, or the like runs at an adjustable distance from a fixed member (or they may be pressed together by springs) and between the fixed member and the casing a space remains to form a return passage for the liquids back to the emulsifying zone.—(Hildebrandt, Brit. 284,354 (1928).)

(32) A rotating disc runs between two fixed ones, the former being provided with ports and the latter with recesses ; in the ports are inclined blades of alternative hand in successive outward rings, so that the material after entering near the axis passes from one side of the disc to the other several times and exhausts through a passage at the periphery.—(Rands and Alexander, Brit. 341,193 (1929).)

(33) The fluids are forced through a series of superposed spaced plates which are provided with grooves on one side; small apertures extend from some of the grooves through the plates, but no two apertures are opposite each other.—(Moore, Brit. 350,716 (1930).)

(34) In an emulsifier of the disintegrator type, the runner is provided with separate inlets for the two fluids and is arranged to deliver them to the grinding space in a number of subdivided alternating streams.—(Loomis, U.S. 1,935,884 (1933).)

(35) Two series of radiating spokes are oppositely or relatively rotated on separate shafts. The rotors are enclosed in a casing suitable to resist pressure, the inlet being axial and the outlet at an intermediate radius.—(Shropshire, U.S. 1,983,782 (1934).)

(36) A rotary grinding element comprises a rim portion having a lateral or frustro-conical peripheral grinding surface connected by a flexible support to a hub portion, the support being arranged in the plane of the grinding surface or in the plane of the smaller peripheral edge of the grinding surface, or between the plane through the centre of gravity of the rim portion perpendicular with the axis of rotation and the plane of the grinding surface or the plane of the smaller peripheral edge of the grinding surface.—(Myers, Brit. 423,403 (1935).)

(37) In a conical mill the liquids are passed through the interstitial conical annular space between rotor and stator elements of conical form, one of which surrounds the other of plug-like form and which are relatively rotatable about their common axis, the annular space being charged with balls adapted to roll upon the oppositely disposed peripheral surfaces.—(Bristow and Pope, Brit. 422,628 (1935).)

(38) In a mill, where the disks are carried in carriers, one of the disks has rigidly secured thereto a plurality of members which extend from the non-operative face of the disk and are mounted in the corresponding carrier for axial movement parallel with the axis of rotation, the disk being spring biased to move toward the other disk with a floating action.—(Kemp and Leggett, Brit. 455,890 (1936).)

(39) High-speed rotating member throws the liquids against a surface from which it rebounds in a clearance space between the rotating member and the surface in a state of turbulence and is simultaneously sheared by edges moving parallel with the surface.—(Holdsworth, Brit. 495,107 (1938).)

Other colloid mills are described in the following selected patents:

Tolman	U.S. 1,987,724 (1935)	Morehouse	U.S. 2,147,821 (1939)
Rafton	U.S. 1,987,944 (1935)	Thüringische Zellwolle A.-G.	Fr. 844,063 (1939)
Crane	U.S. 2,072,710 (1937)		
Heath and Minger	U.S. 2,153,537 (1939)	Butler	U.S. 2,221,342 (1940)
Wynn	U.S. 2,143,099 (1939)	Dixon	U.S. 2,201,889 (1940)

HOMOGENISATION

Emulsions, whether prepared in the laboratory or in technical practice, usually contain dispersed globules of very different diameters. The process of subsequently reducing these globules to an approximately equal diameter many times smaller than the average previously attained in the emulsion is termed homogenisation, and the resulting product is called a homogenised emulsion.

Homogenised emulsions are obviously advantageous in scientific investigations, and will undoubtedly be employed in future researches much more frequently than hitherto. At the moment, however, their utility is more recognised industrially, particularly in dairy work, where homogenised cream and milk have long been familiar products.[1]

Hatschek [2] has shown that subdivision of emulsified globules demands a force which increases enormously as the size of the globules decreases. Laboratory homogenising apparatus is rather unusual as yet and somewhat unsatisfactory, considering what can be accomplished with modern machines in dairies. Briggs [3] devised a simple type of laboratory homogeniser by means of which he was able to reduce the particles in hand-shaken emulsions from an average diameter of 25μ to 5μ. Repeated homogenisation decreased the average diameter to between 2μ and 3μ. These emulsions then showed greatly increased stability.

Kraemer and Stamm [4] have published graphs showing the size-frequency analysis of emulsions of 5 per cent. benzene in 0·0005 N. potassium palmitate as influenced by passage through a Briggs' homogeniser at low and at high pressures. Although at low pressure benzene-in-water emulsions using soap are more finely dispersed by this homogenisation, similar emulsions using gelatin instead of soap are broken completely. Emulsions stabilised with free fatty acids were partially broken. It would seem that the volatility of benzene is a factor in this connection, and the results depend, therefore, on the pressure maintained in the homogeniser-receiver, the extent of formation and rupture of bubbles and laminæ being important for increasing dispersion. [5] Stamm reports that the efficiency of homogenisation decreases as the amount of dispersed phase is increased in the initial emulsion.

Fischer and Hooker [6] obtained good results in the laboratory by passing coarse-grained emulsions through a pestle and mortar arrangement. The emulsion is poured into a metal funnel, within which is turned a pestle. Upon this pestle any amount of pressure may be exerted by means of a screw at the top. The emulsion passes under hydraulic pressure between the grinding surfaces, which, being bevelled, causes the emulsion globules to be decreased in size before passing through the exit.

In 1892, Paul Marix [7] obtained two French patents in connection with the manufacture of margarine for making emulsions by passing the ingredients under pressure through a fine orifice. Later [8] he proposed that the liquids to be emulsified should be finely divided and intimately mixed by rubbing against a moving surface ; under centrifugal force the liquids passed between a stationary plate and a rapidly-revolving plate. Julien [9] adopted the principle of Marix's patent, but forced the liquids through a *series* of small holes. The subdivision of the globules in an already existing emulsion, *e.g.*, milk, with a view to stabilising it was then conceived by Gaulin.[1] He employed a bundle of capillary tubes, against one end of which a powerful spring pressed a concave valve ball. A pressure of 250 atmospheres was required to force the milk (at 85° C.) through these tubes, whereby homogenisation was successfully achieved.[2] Later, agate was substituted for metal, owing to the excessive wear of the latter.[3]

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[1] See, for example, Bergedorfer Eisenwerk A.-G. Astra-Werke, Ger. 614,666 (1935) ; Knott, U.S. 2,132,854 (1938) ; Submarine Signal Co., Brit. 509,924 (1939) ; U.S. 2,101,103 (1939) ; Dodge, U.S. 2,202,649 (1940) ; 2,210,448 (1940).

[2] *Kolloid-Z.*, **7**, 81 (1910).

[3] *J. Phys. Chem.*, **19**, 223 (1915).

[4] *J. Am. Chem. Soc.*, **46**, 2716 (1924) ; *Colloid Symposium Monograph*, **3**, 251 (1925).

[5] Cf. Svedberg, " The Formation of Colloids " (London, 1921), p. 112.

[6] " Fats and Fatty Degeneration " (N.Y., 1917), p. 24.

[7] Fr. 218,946—7 (1892).

[8] Fr. 221,583 (1892).

[9] Fr. 220,446 (1892), 224,553 (1892).

Schröder and Wrede proposed a similar machine, but substituted for the tubes an agate shaft with spiral grooves cut in the surface, which caused the shaft to revolve as the milk was forced through under a pressure of 150 atmospheres. Schröder [4] later replaced the revolving valve with an adjustable stepped valve in which the face of each succeeding step was closer to the seat, thus providing for a gradual breakdown of the globules.

Whilst the Gaulin homogeniser is extensively used on the Continent, other machines are favoured in America and in Great Britain. American types are the Viscoliser and Colony, whilst British types are the De-Laval, Gardner, Weir and Brotherhood. Similar Danish machines are the Rannie and the Jensen-Andersen. The British Brush homogeniser is a recent and quite new type.

THE VISCOLISER

Fig. 76 illustrates the Viscoliser. By means of three pistons working successively by the aid of shaft eccentrics, the emulsion is forced under great pressure through an homogenising valve which takes the form of two ground surfaces seating accurately as a drop and lift valve. The emulsion is forced into the homogeniser at a pressure up to 5,000 lb. per square inch, and the valve through which it must pass is gauged with a strong spring which permits a valve clearance of only a few thousandths of an inch. The seating and unseating of the valve take place with great frequency, so that the emulsion passes through the narrow section of the valve with great velocity, and tremendous shearing action is effected.[5]

The coil spring is so designed that easy hand operation permits adjustment of the homogenising pressure, which is shown on a high-pressure gauge. Thus a Manning type with needle valves to control the passage of the emulsion measures the pressure by direct contact of the emulsion being homogenised. Two recent gauges devised to overcome the objections of the usual gauge are the volumetric pressure gauge and the electrical indicator which records pressures related to the power consumption of the homogeniser.

Some homogenisers, *e.g.*, the Colony and De-Laval, possess a safety disc ; in the event of the pressure rising to a predetermined point, a small metal disc becomes punctured and the emulsion passes back to the low-pressure side of the pump.

Viscolisers having capacities of 50, 125, 200, 300, 500, 800 and 1,000 gallons per hour respectively require motors of 2, 5, 7·5, 10, 20, 30 and 40 h.p. to drive them.

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[1] Fr. 295,596 (1899).

[2] Cf. also Bonnet, Fr. 333,501 (1903), and Répin, Fr. 328,064 (1902).

[3] Cf. Talansier, Brit. 19,626 (1909).

[4] Ger. 277,225 (1912).

[5] Smith and Bird, U.S. 2,057,925 (1936).

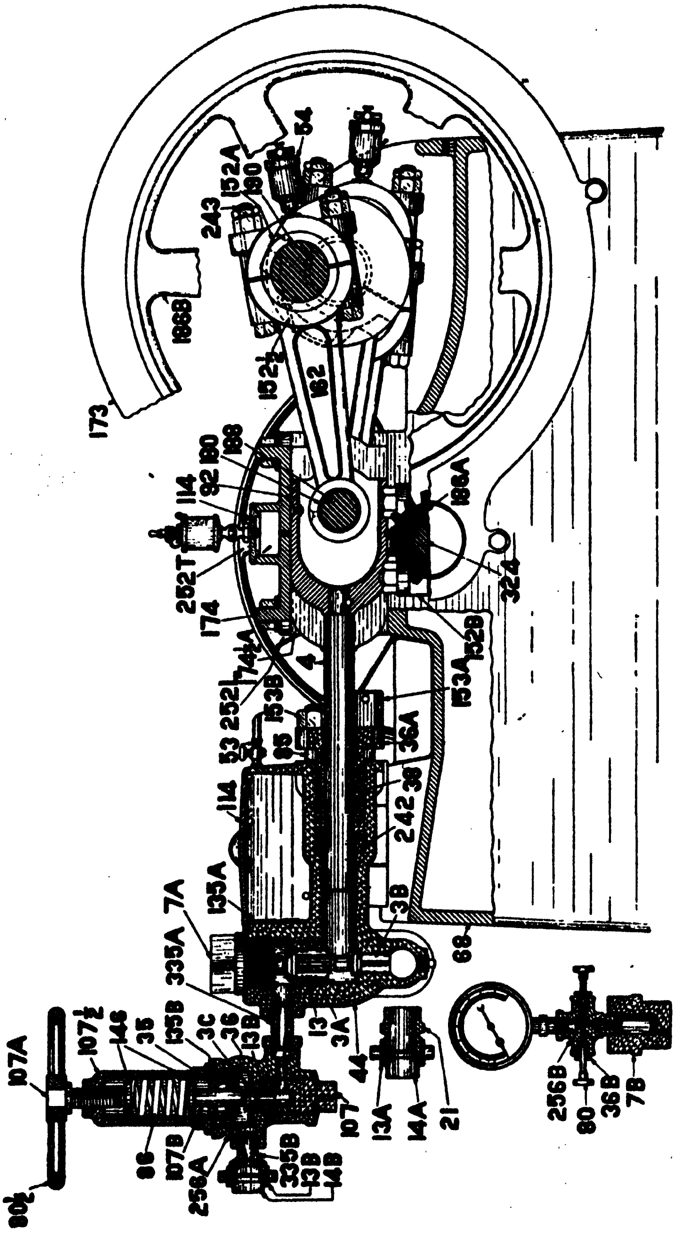

Fig. 76. Sectional View of the Viscoliser.

No.	Part
80½	Hand Wheel.
107A	Regulating Screw.
107½	Viscoliser Valve Hood.
146	Spring-Ends.
86	Regulating Spring.
35	Stuffing Box.
107B	Regulator Plunger.
135B	Viscoliser Valve Gasket.
335A	Nipple.
7A	Plain Valve Plug.
256A	Viscoliser Valve Body.
3C	Viscoliser Valve Disc.
36	P. R. Gland Nut.
135A	Valve Plug Gaskets.
13B	Valve Seat.
35B	Outlet Pipe Adapter Nipple.
13B	Discharge Sanitary Union Nut.
14B	Discharge Sanitary Union Sleeve.
107	Valve Base Plug.
13	Discharge Valve Seat.
3A	Discharge Valves.
44	Bronze Cylinder.
3B	Suction Valves.
68	Power Frame.
13A	Suction Sanitary Union Nut.
14A	Suction Sanitary Union Sleeve.
21	Suction Connection 1½ in. Bronze Pipe Plug.
256B	Needle Valve Body.
80	Needle Valves.
36B	Needle Valve Glands.
7B	Valve Plug Tapped ¾ in.
114	Water Pot Cover.
53	Drip Cocks and Tubes.
85	Bronze Gland Studs.
252L	Loose Pulley.
252T	Tight Pulley.
153B	Upper Gland Nuts.
174½A	Side Guide Plates.
4	Plungers.
174	Top Guide Plate.
173	Gear Guard.
114	Cross Head Oil Well Cover.
92	Cross Heads.
180	Cross Head Pin Bushings.
188	Cross Head Pins.
162	Connecting Rods.
152½	Crankshaft Bearing Caps.
186B	Gear.
243	Connecting Rod Bolts.
152A	Crankshaft Caps.
190	Machined Steel Crankshaft.
54	Grease Cups—¼ in. Shank.
242	Plunger Throats.
38	Plunger Packing (6 rings per plunger).
36A	Plunger Glands.
153A	Lower Gland Nuts.
152B	Gear Shaft Bracket Caps.
324	Gear Shaft.
186A	Pinion.

Great force is required to subdivide a small oil globule,[1] and the power consumption during the running of an homogeniser rises as the working pressure is increased. The following table of the rating of the De-Laval homogeniser illustrates this :—

Size No.	1	2	3	4	5	6	7
Max. capacity (gal./hr.)	33	88	165	310	420	530	770
Max. power consumption (h.p.)—							
At 1,500 lb. per sq. in. pressure	0·8	2·1	3·8	7	10	12	18
At 3,000 lb. „ „	1·5	4·0	7·5	14	19	23	25
At 4,500 lb. „ „	2·3	6·0	11	20	28	34	52

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[1] Hatschek, *Kolloid-Z.*, 7, 81 (1910).

Extreme dispersion of an emulsion is assured; a salad cream with oil globules up to 20μ can be reduced to a smooth product in which all the globules are less than 1μ and most from 0·1μ to 0·2μ. Air is not whipped in, as with colloid mills. Such homogenisation is due to pronounced shearing, caused by high velocity flow through the valve, and actual subdivision of the globules by impact on the wall of the valve head.

Sibree [1] investigated emulsions of paraffin oil in aqueous sodium oleate solutions, the emulsions being viscolised in the present writer's laboratory. At an homogenising pressure of 2,000 lb. per square inch, and using viscous paraffin, Sibree found that "no particles were above 8μ in diameter and 90 per cent. of the particles were below 2μ in diameter." Using limpid paraffin the homogenised emulsion contained the globules so small that a size-frequency analysis was impossible; only a few globules reached a diameter up to 2μ.

TWO-STAGE HOMOGENISATION

A phenomenon frequently encountered with homogenised emulsions is that of clustering of the globules.[2] The clusters are numerous and contain up to several hundreds of globules. With milk enriched with cream and then viscolised, clustering occurs at 2,000 lb. per square inch pressure and increases at higher pressures. Such clustering leads to creaming of an emulsion, and it is obviously desirable to destroy this tendency. Accordingly, it is now usual to carry out a two-stage homogenisation, passing the emulsion directly from a first valve operating at 3,000—5,000 lb. per square inch to a second valve set at 1,000 lb. per square inch.[3]

The Colony two-stage homogeniser is illustrated in Fig. 77. The liquid to be treated is drawn from the supply line into the triple cylinders A at atmospheric pressure. The plungers B put this emulsion under high pressure and force it through pump valves at C into the communicating port D, which leads to the first stage homogenising valve. Here the emulsion forces its way through the minute opening between the homogenising valve E and its seat F. After first-stage homogenisation the emulsion passes through L to a second homogenising valve, identical with the first in its design. Finally the emulsion is discharged.[4]

The sizes and power consumption of the Colony two-stage homogeniser are as follows, the size motors being listed for operating the homogeniser

Size.	Motor H.P.
60	3
100	5
250	10
500	20

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[1] *Trans. Faraday Soc.*, **27**, 170 (1931).

[2] Clayton, "Colloid Aspects of Food Chemistry and Technology" (London, 1932), pp. 220, 231, 237, 257, 266.

[3] A multi-stage homogeniser is described by Ordway, U.S. 2,137,854 (1938).

[4] Cf. Hellerud *et al.*, Brit. 365,586 (1930).

up to 4,000 lb. pressure ; if a pressure of 2,000 lb. is required, only one-half the power listed is necessary. (Size = gallons per hour.)

Instead of using two separate and identical valves, the modern Viscoliser is fitted with a so-called Duo-Visco valve. This is a single unit in which the valve can be set for any working pressure. The emulsion on leaving the valve itself (Fig. 78) has to pass a narrow annular passage of such dimensions as to impose a pressure of about 1,000 lb. per square inch. This passage is effected by means of a breaker ring around the valve.

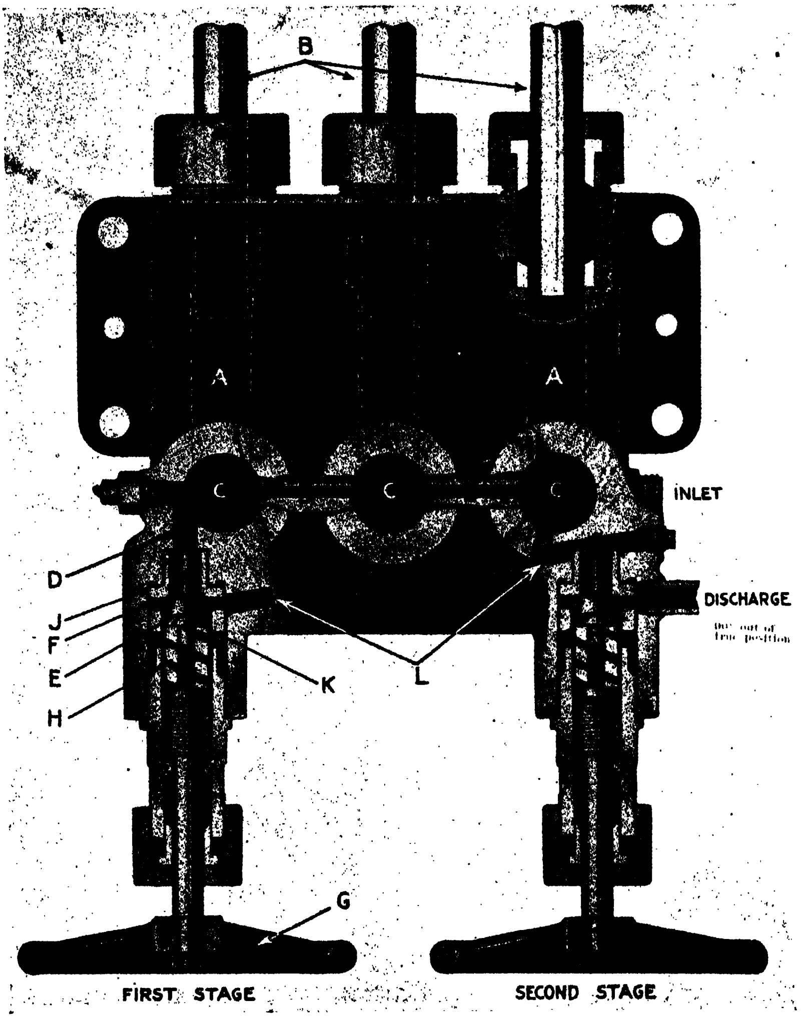

Fig. 77. The Colony two-stage homogeniser.

Homogenisation produces a great increase in viscosity[1] of an emulsion (see p. 403), due to the enhanced adsorption of emulsifying agent at the newly-formed extensive oil/water interface. It is significant that the second stage homogenisation greatly reduces this viscosity (and, in fact, four or more stages are sometimes employed). The probable explanation for the destruction of clusters of globules and for the consequent decrease in viscosity is that in the first stage homogenisation the oil globules are entangled in films of denatured protein or saponin, the second stage

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[1] Note the conclusion of Leviton and Leighton, *J. Phys. Chem.*, **40**, 79 (1936), that the viscosity of a suspension is independent of particle size and that any deviation from this relationship is to be attributed to the amplification of the volume of the suspended material by the medium.

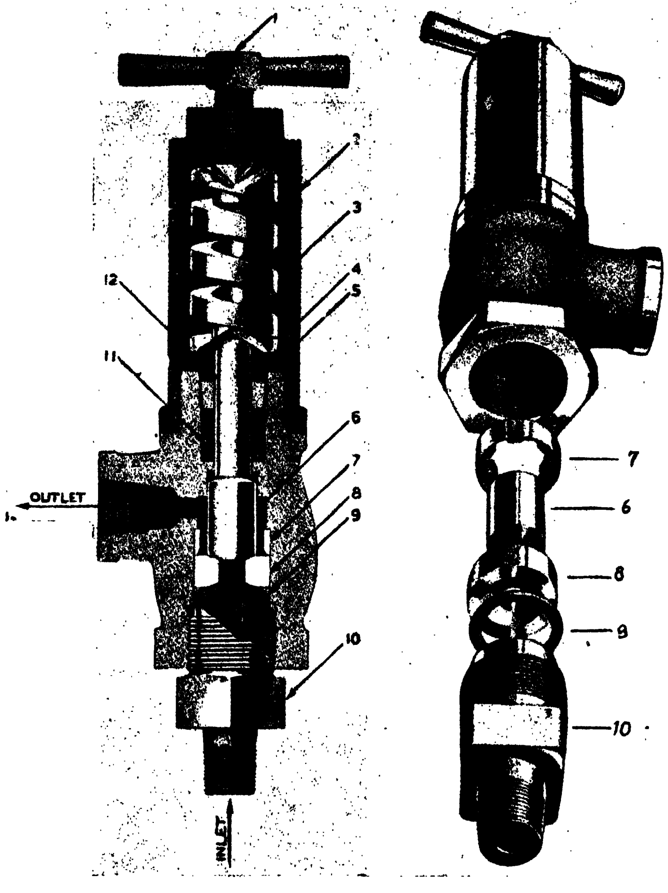

FIG. 78. The Duo-Visco valve.

1. Adjusting Handle to Adjust Pressure.
2. Valve Bonnet.
3. Pressure Spring.
4. Spring End Cup.
5. Packing Gland.
6. Double-end Viscolising Valve.
7. Breaker Ring and Guide.
8. Double Valve Seat.
9. "Blow-Proof" Gasket for Bottom Plug.
10. Bottom Plug.
11. Valve Stem Packing.
12. Valve Stem.

(effecting no further degree of dispersion) simply loosening these films. Such an explanation seems sound, for the present writer has only observed two-stage homogenisation of value in the treatment of milk and salad creams, where proteins are the emulsifying agents ; emulsions stabilised with gums or emulsions of bituminous material in dilute alkaline solution show no clustering of globules and no decrease in viscosity when given a second homogenisation.

THE JENSEN-ANDERSEN VALVE

A familiar homogeniser in Continental works is the Jensen-Andersen machine, which incorporates a valve of special design. Fig. 79 illustrates this valve, which comprises two plates in contiguous and opposed relation, each plate having a series of concentric or eccentric ribs or rings which mutually interfit and between which the emulsion is forced[1] (see Fig. 80).

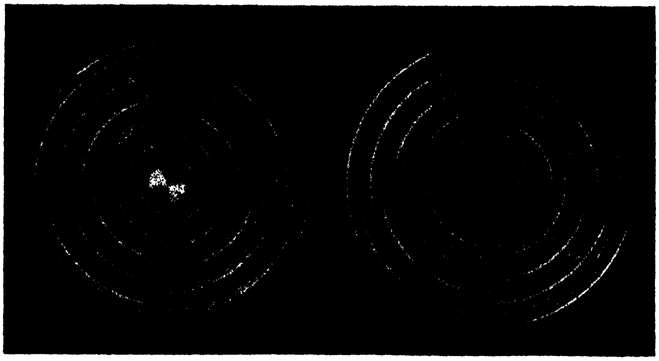

FIG. 79. Faces of the Jensen-Andersen valve.

A typical valve examined by the present writer showed the valve itself to have five rings, 0·05 inch deep and 0·075 inch pitch. The total diameter was 0·985 inch and the length was 0·75 inch. The valve seating had six rings of the same depth and pitch as the valve itself. The minimum diameter of the emulsion duct leading to the faces was 0·15 in. The overall length of the valve and seating was 3·5 inch.

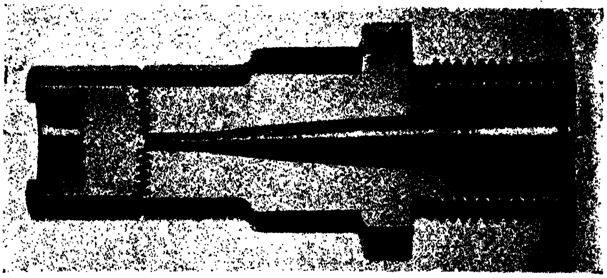

FIG. 80. Section through the Jensen-Adersen valve.

It is claimed that more intensive homogenisation is secured by the use of this type of valve. A closely related idea is that of Bendixen and Wood,[2] who claim a homogeniser of the pump type wherein the labyrinth is formed between a plug having a roughened surface and a conical seat.

THE IMPULSOR EMULSIFIER

This useful machine is classed with valve homogenisers. It was developed after laboratory work by Frazer and Walsh,[3] who required finely-dispersed emulsions for biological research (see p. 261). The basic principle of the apparatus is the use of a pulsating action by which the liquid phases to be emulsified are subjected to alternate decreases and increases of pressure before being ejected at a very high velocity through a narrow gap. The liquids are drawn into and intimately mixed in the cylinder by the suction action of a plunger ; disintegration is then effected by the shearing force exerted during expulsion through the gap. With emulsions of 20 per cent. of olive oil in 5 per cent. aqueous solution of gum arabic, Frazer and Walsh observed that the globules of oil averaged ½—1μ diameter.

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[1] Brit. 129,279 (1920).

[2] Brit. 413,252 (1934).

[3] *J. Physiol.*, 78, 467 (1933); Walsh and Collins, Brit. 323,534 (1928); Walsh, U.S. 1,780,853 (1930).

Fig. 81 illustrates the Impulsor emulsifier. It consists of a cylinder, C, having two inlets, A, and an outlet head, D, within which a plunger. B, is made to reciprocate by means of a crank drive, G. The two phases of the emulsion can be fed in separately in desired volume ratio. At the suction stroke of the plunger B some of the mixture is drawn into the cylinder through a non-return valve, which closes on the return stroke of the plunger. Pressure increases until it reaches a value predetermined by adjustment of the compression of the powerful outlet valve spring by means of the handwheel F. When this pressure is attained, the outlet valve D opens and a portion of the mixture is ejected at high velocity between the valve face and its seating.

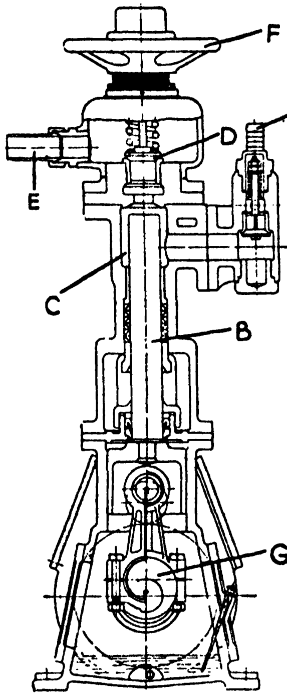

Fig. 81. The Impulsor emulsifier.

The machine runs at 275 r.p.m. and the liquids within the cylinder are subjected to cycles of compression and expansion at a corresponding rate, and in consequence undergo violent agitation. High output is combined with low power consumption. For an output of 100 gallons per hour of normal emulsion the machine requires only a 2¼-h.p. motor.

THE "BRUSH"-HOMOGENISER

This recent machine[1] consists of a three-throw pump delivering the emulsion under pressures adjustable up to 4,000 lb. per square inch, through the homogenising valve to the delivery line. The new feature is the valve (Fig. 82), which is, in principle, a tube of specially selected metal, B2, threaded over and centred upon a horizontal spindle, B0. This construction provides homogenising surfaces, one stationary and the other free to expand, being attached to the tube itself. (Fig. 83).

Between the two faces, homogenising valve rings of special design and material may be placed, the number of rings corresponding to different commodities and to degrees of homogenising effect required. The stationary surface referred to is ground upon the bush, B1, while the moving surface is denoted by the symbol B3 on the sectional drawing.

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[1] Brit. 420,437 (1933); 528,019 (1939).

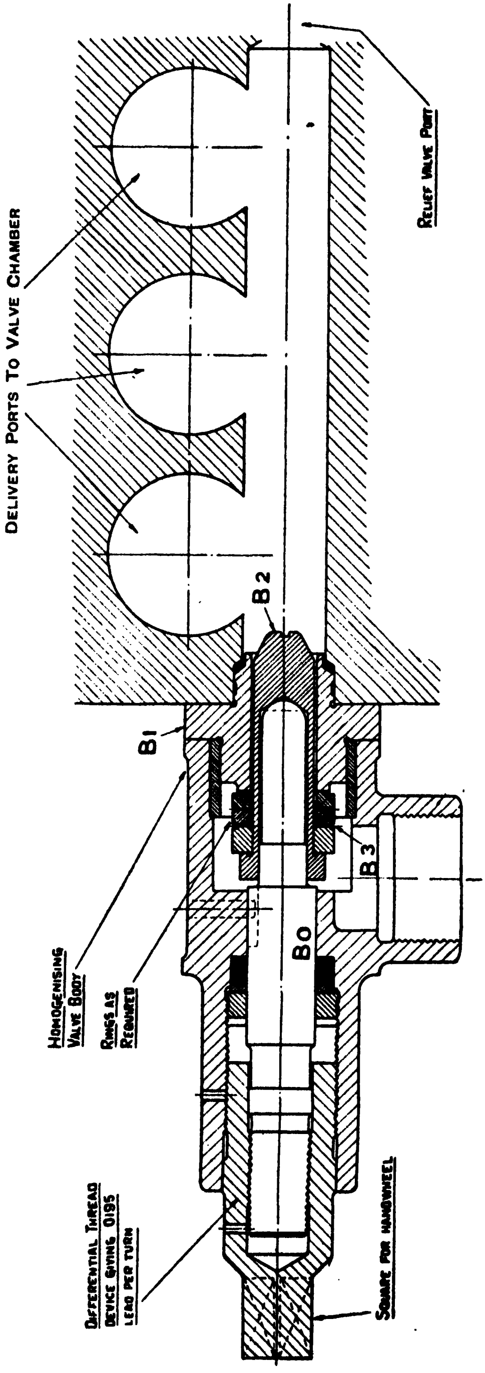

FIG. 82. Section through the Brush homogenising valve.

A differential thread is located between the items marked " J " ; the thread being machined to give, when adjusted, 0·0195 inch per turn. The sequence of operation is as follows :—

Liquid is delivered from the discharge ports of the pump component of the homogeniser to the chamber in which the tube threaded over its rod, B2/B0, is located. The quantity, as a function of the pump speed, then raises pressure in the homogenising chamber. This procedure, being directed through the cone entry of item, B1, exerts a force on the homogenising faces, stretching the tube B2 over its central rod, and so providing an aperture between the homogenising faces at B3/B1.

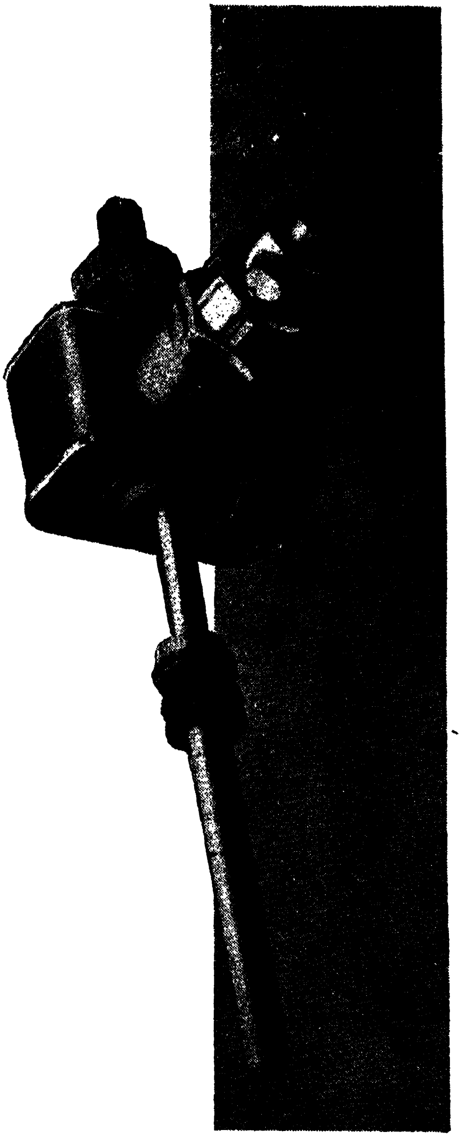

FIG. 83. Assembly of the Brush homogenising valve.

The amount of stretch possible in the valve, and therefore the aperture desired—as a function of the pressure—may be set at will, by adjusting the position of the rod by means of the differential thread, to establish a datum.

Such a valve has no inherent inertia, and variations in suction head are taken up by the contraction/expansion of the special tube B2. This operation is practically instantaneous, and consistent homogenising results are attained.

HOMOGENISED MILK

Probably the best technical illustration of the effect of fine subdivision is the familiar homogenising of milk or cream.[1]

When milk at 90° F. or at 145° F. is homogenised at a pressure of 1,500 lb. per square inch, no cream layer forms on subsequent storage. The warmer the milk the smaller are the fat globules. There is no change in density, but the viscosity of raw milk is increased and that of pasteurised milk decreased by the homogenisation. The titratable acidity increases due to lipase action, avoided by pasteurisation prior to homogenisation. A notable feature in homogenised milk is the enhanced sedimentation, due to the absence of the rising, larger fat globules.

The temperature at which homogenisation is conducted influences the size-frequency analysis, rise in temperature shifting the peak of the percentage of globules towards the small globules. The following table is due to Rahn.[2]

TABLE 49

INFLUENCE OF TEMPERATURE ON HOMOGENISATION

Diameter-Range of Fat Globules.	Homogenisation Conducted at		
	20° C.	40° C.	65° C.
μ	Percentage of Total Milk Fat.		
0—1	2·3	1·9	4·3
1—2	29·3	36·7	74·4
2—3	23·3	21·0	9·0
3—4	29·8	25·2	12·3
4—5	*Nil.*	15·2	*Nil.*
5—6	15·4	*Nil.*	*Nil.*

The stability of homogenised milk with respect to the separation of the butterfat has been studied by Sobbe.[3] Two samples of milk were homogenised and allowed to stand in a measuring cylinder at room temperature for seventy-two hours, a little formaldehyde being added as preservative. Analysis of the fat contents at different levels were then made, and the following results obtained :—

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[1] Babcock, U.S. Dept. Agr., *Tech. Bull.*, **438**, 11 pp. (1934); *Dairy World*, **13** (vii), 33; **54** (1934); *J. Milk. Tech.*, **2**, 26 (1939); Dorner and Widmer, *Lait*, **11**, 545 (1931); Trout, Halloran and Gould, Mich. Agr. Expt. Sta., *Tech. Bull.*, **145**, 3—34 (1935); Gould and Trout, *J. Agr. Research*, **52**, 49 (1936); Reid, *Milk Dealer*, **28** (ix), 56 (1939); Doan, *J. Milk. Tech.*, **1** (vi), 20 (1938); Tracy, *Milk Plant Monthly*, **24**, (iv) 28 (1935); Mohler, *Proc. 11th Ann. State Coll. Wash. Inst. Dairying*, **1938**, 118.

[2] *Milchwirtschaft. Forsch.*, **2**, 382 (1935). See also Whitaker and Hilker, *J. Dairy Sci.*, **20**, 281 (1937), on "Homogenisation at Different Temperatures."

[3] *Milchw. Zentr.*, **43**, 503 (1914).

Sample.	Milk A.		Milk B.	
Initial Fat Content.	2·6 per cent.		3·3 per cent.	
Per cent.	Raw.	Homogenised.	Raw.	Homogenised.
Fat in lower, 50 c.c. .	0·3	2·3	0·2	2·95
Fat in middle, 50 c.c. .	1·4	2·5	0·6	3·20
Fat in upper, 50 c.c. .	8·5	2·9	14·5	3·85

Very little creaming takes place in the case of homogenised milk, whilst raw milk creams rapidly. Even centrifugal separation has but little effect on homogenised milk. Thus, Burr and Weise[1] found that whilst homogenised milk retained from 72·7 to 87·5 per cent. of the total fat after centrifuging, raw milk under similar treatment only retained from 3·8 to 7·3 per cent. of its total fat. The deformation of the fat globules has been studied by Baldwin.[2]

Cream is frequently homogenised, but skim milk cannot be homogenised. Homogenised milk cannot be churned into butter, and homogenised cream cannot be "whipped"; the addition of a colloid, such as gum tragacanth, is necessary if a permanent foam is desired. The Brownian movement of the fat globules is very marked, whilst there is a measurable decrease in the surface tension.[3]

The cause of these remarkable changes is the increased adsorption of milk proteins (notably casein) on the fat globules.[4] Since in the homogenised products, the number of fat globules has increased about a thousand times, the adsorbing interface created is enormous. The adsorption of casein is at once manifested by the large increase in viscosity, homogenised milk and cream being much thicker than the original liquids. Wiegner[5] reduced the average diameter of the fat globules in milk from 2·9 μ to about 0·27 μ, and from viscosity measurements calculated that, of the casein in milk, 2·27 per cent. was adsorbed in the ordinary sample and 25·2 per cent. in the homogenised milk. (This is based on the assumption that only casein is adsorbed and that the mean thickness of the adsorbed layer is 6·8 mμ.) That adsorption is the main factor in homogenised emulsions has been demonstrated also by Briggs.[6]

Wiegner[7] has investigated the change in the diameter of the fat

[1] *Molkerei-Ztg.* (Hildesheim), **28**, 367, 381 (1914).

[2] *Am. J. Pub. Health*, **6**, 862 (1916).

[3] This effect is still open to investigation. Webb found that the surface tension of homogenised *cream* was *increased*; *J. Dairy Sci.*, **16**, 369 (1933).

[4] Webb, U.S. 2,010,573 (1935), uses this phenomenon to isolate milk proteins.

[5] *Kolloid-Z.*, **15**, 105 (1914).

[6] *J. Phys. Chem.*, **19**, 229 (1915); cf. Martici, *Arch. d. Fisiol.*, **4**, 133 (1907).

[7] *Kolloid-Z.*, **15**, 105 (1914); cf. Rousseau, *Le Nourrison*, **2**, 237 (1923).

globules and the increase in their numbers when milk is homogenised. The following were the results obtained :—

Sample.	Density.	Per cent. Fat.	Diameter of Fat Globules.		Number of Fat Globules per 100 c.c.	
			Normal.	Homogenised.	Normal.	Homogenised.
1	1·0313	3·17	$\overset{\mu}{2{\cdot}86}$	$\overset{\mu}{0{\cdot}27}$	2·87 × 10^{11}	3·41 × 10^{14}
2	1·0320	2·87	2·94	0·17	2·40 × 10^{11}	3·02 × 10^{14}

The number of particles in the first sample has increased 1,188 times, and in the second sample 1,258 times, after homogenisation. The surface area of the fat globules has been increased 112 and 117 times respectively. The viscosities of the samples of raw and homogenised milks were in the ratio of 1 : 1·12 and 1 : 1·15 respectively. There was no apparent change in density and no difference in electrical conductivity, although Buglia,[1] in similar work, noted a slight increase in electrical conductivity consequent on homogenisation. Both Wiegner and Buglia report a slight decrease in osmotic pressure after homogenisation.

In the United States of America the term " viscolising " is usually substituted for " homogenising." There, a practice has been common of separating some or all of the cream from milk, viscolising such cream, and then remixing it with the residual milk or skim milk. The resulting milk then gives rise to a greater volume of cream on standing, the milk in consequence seeming very rich in fat.

Now ordinary whole milk on homogenisation does not yield a bigger cream layer; it is essential to viscolise cream and mix this with the milk. Thus, Martin and Combs [2] viscolised a sample of milk at 2,000 lb. pressure and found that the volume of cream rising was 2 per cent., whilst the raw milk gave a cream volume of 10 per cent. On separating milk containing 4 per cent. fat and viscolising the cream and then reconstituting the milk the data given in Table 50 were obtained relating to cream rising.

Whilst offering no explanation for these results, the authors conclude " the fundamental cause in creaming ability of milk will possibly be found in the milk serum, and not the butterfat, as has long been the opinion."

Doan [3] has made an extensive study of viscolised reconstituted milk, being concerned with discovering a method for its detection. An examination of viscolised milk under the microscope showed the fat to be present as minute globules, " but gathered together into clumps containing hundreds of small globules. These clumps were extremely numerous, quite large in size and of irregular shape resembling flecks of foam. No normal globules were observable." Photomicrographs support Doan's statements.[4]

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[1] *Ibid.*, **2**, 353 (1908); cf. Touschot, *Rept., Min. Agr. Prov., Quebec* (1908), 184.

[2] *J. Dairy Sci.*, **7**, 202 (1924).

[3] *Ibid.*, **10**, 501 (1927).

[4] *Vide* also Mortensen, Iowa Agr. Expt. Sta., *Bull.*, **180** (1918); Sherwood and Smallfield, *J. Dairy Sci.*, **9**, 68 (1926); Reid and Moseley, Missouri Agr. Expt. Sta., *Res. Bull.*, **91** (1926); Dahle, *Ice Cream Trade J.*, **26**, 55 (1930).

It was further observed that although the volume of the cream on viscolised reconstituted milk is so great, the concentration of fat in the cream layers is much less than in the cream on ordinary milk. In each case, the skim milk below had approximately the same fat content. Pasteurisation of viscolised reconstituted milk brought about a decrease in size of the " visco-clumps " and there was a greater number of individual small globules. The cream volume, which rises after pasteurisation, is still much greater in the case of the viscolised sample, though not so pronounced as in the unpasteurised sample.

TABLE 50

VOLUME OF CREAM RISING ON PASTEURISED MILK MADE FROM VISCOLISED CREAM AND UNTREATED SKIM MILK

Treatment.	Temperature °C.	Per cent. of Total Volume appearing as Cream Hourly after Standing. Hours.											
		1	2	3	4	5	6	8	10	12	14	16	18
Raw milk before separation, 4 per cent. fat . .	50	10	11	11	11	11	11	12	12	12	13	13	14
	35	10	13	18	21	21	21	21	21	21	21	20	20
Pasteurised milk made from 45 per cent. cream viscolised 2,500 lbs., 4 per cent. fat .	50	10	25	26	26	26	25	25	24	24	23	22	22
	35	0	0	31	31	31	31	30	29	29	29	28	27

Doan points out that it is not the fat content of the cream undergoing viscolisation, but the actual amount of cream so treated which is the important factor. " This would suggest that homogenisation sets up a structure of some sort among the " visco-clumps " of fat in the cream and that the volume of this structure depends on the available space at the time of homogenisation, and further that this structure maintains, to a certain extent, its volume upon dilution of the cream with fluid milk or skim milk." Here the author leaves the matter.

Undoubtedly what happens is that homogenisation of the cream, which is so rich in milk proteins already adsorbed on the fat globules, still further increases the adsorption of protein due to the now greater fat/aqueous interface. Some sort of foam-like structure is possible if the adsorbed protein is " precipitated " as mechanical surface aggregates (Ramsden). This structure will rise practically as a whole, owing to its lower density, when mixed with milk. No data are available regarding the gas content of the viscolised cream, although this factor is also important in the phenomena described above.

Later, Doan[1] has published a lengthy account of further work on the problem. Mixtures were made from cream and milk or skim milk to the desired composition and exact analytical checks carried out.

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[1] *J. Dairy Sci.*, **12**, 211 (1929).

The fat content of the mixtures ranged from 3 per cent. to 16 per cent., and homogenisation was conducted at 38° C. at a pressure of 3,500 lb. Clumping of the fat globules was followed by the microscope, and the factors involved were studied as follows : (*a*) fat concentration, (*b*) homogenising pressure, (*c*) heat-treating the plasma, (*d*) acidity.

The following table, due to Doan, illustrates the general phenomenon under investigation :—

TABLE 51

INFLUENCE OF FAT CONTENT ON HOMOGENISATION RESULTS

Sample.	Fat (per cent.).	Microscope Appearance of the Fat.	Cream Layer 48 hrs. at 10° C.	Fat in Upper Layer of Cylinder (per cent.).	Cream Layer on Diluted Sample 48 hrs. at 10° C. (per cent.).
1	4·2	Well dispersed—no clumps	*Nil.*	4·3	*Nil.*
2	7·2	Clumping tendency . .	,,	7·15	,,
3	9·5	Evident clumping . .	,,	9·7	16·0
4	11·0	Very evident clumping .	,,	11·0	20·5
5	13·5	Prominent clumping. .	,,	13·6	39·0
6	16·1	Pronounced clumping .	,,	16·3	68·0

In all cases the "Diluted Sample" means that the original sample was diluted with skim milk to a standard fat content of 3 per cent.

It was found that "when other things are constant, the degree of fat-clumping increases with the concentration of the fat in the mixtures," thus agreeing with Hening,[1] who found marked clumping for those mixtures containing over 10 per cent. of fat. The study of the influence of the pressure employed during viscolising showed that clumping began when 2,000 lb. was developed, and increasing the pressure to 3,000 or 4,000 lb. gave pronounced clumps in the mixtures so treated.

Interesting data were obtained by Hening[2] in an investigation concerning the homogenisation of ice cream mixes, using a Manton-Gaulin two-stage machine. Mixes prepared without gelatin were homogenised at first-stage pressures from 4,000 to 1,000 lb., decreasing at 500 lb. intervals with a constant pressure of 500 lb. on the second stage ; they showed a gradual decrease in viscosity from 4,000 lb. to zero pressure. Homogenisation with the first stage fixed at 2,500 lb. and decreasing the second stage pressure from 2,000 to 500 lb. at 500 lb. intervals, showed different results. The 2,000 lb. second-stage pressure gave more viscous mixes with larger fat globule clumps than in the case of the mixes homogenised with a greater pressure difference between the stages.

Various investigators[3] have shown that not only does the heating of milk destroy the creaming capacity of milk, but that this effect is more pronounced if the milk plasma is heated. Doan followed the effect of heating the *milk plasma* on the degree of clumping of the subsequently homogenised mixtures.

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[1] *Ibid.*, 11, 299 (1928).

[2] *Ibid.*, 19, 714 (1936).

[3] Palmer and Anderson, *ibid.*, 9, 1 (1926); Troy and Sharp, *ibid.*, 11, 189 (1928).

"A portion of fresh raw skim milk was divided into two parts, one of which was heated to 82·2° C. for ten minutes and cooled. Fresh raw cream containing 53·4 per cent. fat was then standardised to approximately 12 per cent. fat, using the raw skim milk and again using the heated skim milk. Two other mixtures of approximately 13 per cent. fat were compounded in the same way." Doan then homogenised these four mixtures as usual at 38° C. and observed a reduction in the fat-clumping in the two mixtures containing the heated plasma.

The effect of changing the acidity of the mixture to be viscolised was surprisingly slight, and led the author to conclude that the fat-clumping was but little connected with the electrical charge carried by the fat globules.

The thermal stability of homogenised cream in its relation to "feathering" or "precipitating" in coffee or tea has been studied by Webb and Holm.[1] An increase in the pressure of homogenising the cream reduced the time for coagulation to occur in heating to 120° C. The acidity of the cream is the main factor involved in thermal stability. The two effects are probably related to the condition of the protein content of the cream, homogenisation and acidity both tending to "precipitate" adsorbed protein.

This is borne out by the extensive results of Jenkins and Mack, who have listed a number of factors which are concerned in the oiling off of cream.[2] Thus, partially frozen milk, when separated, gives a cream which produces an oily separation in coffee. Again, prolonged holding of cream at the pasteurisation temperature increases the amount of destabilised fat in cream. "Pumping cream from pasteuriser to cooler by proper size centrifugal pumps had no effect on the fat emulsion, while the use of oversize pumps destabilised the fat to some extent. Steam piston pumps do not affect the fat emulsion adversely; in fact, with cream which oiled off badly, the piston pumps partially re-emulsified the fat which had separated."

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[1] *Ibid.*, **11**, 243 (1928); cf. Burgwald, *J. Agr. Research*, **26**, 11 (1923).

[2] *Ibid.*, **20**, 723 (1937).

CHAPTER XII

DE-EMULSIFICATION

Whilst the problem of making stable emulsions figures prominently in many industrial operations, the converse problem of " breaking " emulsions is also important. Only too frequently emulsions are found as undesirable factors in certain technical processes, and methods for their de-emulsification or separation demand much thought and ingenuity. Just as no absolutely general rule can be formulated for making any kind of emulsion at all, so no general rule obtains for breaking any given emulsion. Each system presents its own inherent difficulties, so that where a certain scheme operates successfully with some emulsions the same scheme may be quite ineffective for other emulsions.

Well-known examples where de-emulsification is employed are the separation of water from crude petroleum emulsions, the separation of water from water-gas tar emulsions, the separation of oil from condenser water and the recovery of wool fat from wool-scouring liquors.

BREAKING CRUDE-OIL EMULSIONS

More attention has been given to the problem of breaking or resolving crude oil-field emulsions than to any other case of de-emulsifying technical emulsions. The breaking of such systems, frequently very stable, has resulted in the development of many processes, which, however, fall into three main classes [1] : mechanical or physical methods, chemical methods, and electrical methods.

MECHANICAL METHODS

Emulsions of water in light petroleum oils are not so stable as those in heavier oils and frequently resolve into oil and aqueous layers simply because of the difference in density of the two phases.[2] Gravity separation is influenced also by such factors as viscosity of the oil and the nature and quantity of the emulsifying agent. Standing the crude-oil emulsion in sumps (the " sunning process ") may demand considerable time to effect stratification, with consequent losses of the more volatile fractions of the oil. The use of special plant, such as incorporating inclined baffles,[3] serves to minimise the size of the settling vessels, an expensive item. Imparting a relatively rapid, short oscillatory motion at right angles to the direction of flow of the emulsion is claimed by Palmer,[1] whilst Jones[2] claims weirs of sinuous form.

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[1] Summaries are given by: Berkman and Egloff, " Emulsions and Foams " (New York, 1941); Shea, U.S. Bur. Mines, *Bull.*, **417** (1939), pp. 106; Furst and Both, *Bohrtech.-Ztg.*, **1935**, 310; Monson, *IIe Congr. mondial petrole*, 2, Sect. 2, *Phys. chim. raffinage* (1937), 335—343; Kusakov, Kuznetzova and Semenenko, *J. Tech. Phys.* (*U.S.S.R.*), **4**, 1877 (1934); Dumitrescu, *Analele minelor Romania*, **17**, 101 (1934); Valentine and McLean, *Refiner and Natural Gasoline Mfr.*, **14**, 32 (1935); Fortine, *Oil Gas J.*, **35** (xi), 71; (xii), 42 (1936); van Dedem, *ibid.*, **36** (xiii), 65 (1937); Dow, U.S. Bur. Mines *Bull.*, **250** (1926); Uren, *Natl. Petroleum News*, **21** (xiii), 51; (xvi), 59; (xx), 61; (xxvii), 59 (1929); Lottermoser and Calantar, *Kolloid-Z.*, **48**, 179 (1929); Koetschau, Liesegang's " Kolloidchemische Technologie " (Dresden, 1932), p. 806; van der Minne, *Proc. World Petroleum Congr.* (London, 1933), p. 516.

[2] *Vide* Pink, U.S. 1,698,002 (1929); 1,698,067 (1929); Mahone, U.S. 1,940,762 (1933); Edwards, U.S. 1,968,131 (1934); Barber, U.S. 1,945,766 (1934); Linnmann, U.S. 1,671,115 (1928) and Brit. 291,608 (1927).

[3] Fisher, U.S. 1,940,794 (1933). See Erfurt, Brit. 361,728 (1931).

Centrifugal removal of water is an obvious suggestion, but its application, according to Dow, has been confined to special crudes such as those from the Mid-Continent American fields. Centrifuging is often advantageous in the treatment of bottom settlings. Sometimes two centrifugal treatments are indicated and heating may be an advantage, *e.g.*, lowering the viscosity of the oil. The density of the oil is, of course, an important factor in deciding the merits of centrifugal treatment, *e.g.*, some Californian and Mexican crudes have densities close to that of water. Another factor to be considered is the sand and dirt carried in the crude oil, their accumulation in the centrifuge demanding more or less frequent cleaning.

Heat is often employed prior to gravity separation,[3] the decreased viscosity of the oil when hot being helpful in permitting coalescence of the water globules. Temperatures as high as 120° C. must be maintained with stable crude oils. Heating under pressure is also practised,[4] *e.g.*, oil after preheating (65° C.) is raised to 245° C., water vapour and distillate being removed and condensed under pressure. Elliott[5] heats the emulsion under superatmospheric pressure and then introduces it under pressure into a closed settling zone, where it cools off, the final pressure being then subatmospheric. Heating may also be applied after the addition of suitable electrolytes,[6] *e.g.*, ammonium sulphide.[7]

A development in the heat-breaking of these emulsions is the National Oil-Rator, which operates without losses due to evaporation.[8] The essential equipment (Fig. 84) consists of (1) a thermostatically controlled gas-burning heater, and (2) a heat exchanger to cool the de-emulsified oil and to preheat incoming emulsion. Thus, the emulsion is passed through a 10-section unit wherein its temperature is raised to about 98° C., and it is then run into a " gun barrel," where the first separating water settles out. The first unit is operated under about 30 lb. pressure. The fluid is now conducted through two further units connected in parallel, the temperature rising to about 150° C. This is sufficiently high to vaporise the remaining water, and separation of the steam and oil is made in a " flash chamber." As the flash point of the oil is about 205° C., steam may be vented to the atmosphere without loss of the volatile fractions of the oil. The second two units operate under about 10 lb. pressure.

Various modifications of heating processes are claimed, such as: (1) heating the emulsion while descending a spiral conduit, the oil being

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[1] U.S. 1,781,076 (1930).

[2] U.S. 1,920,468 (1933).

[3] Smith, *Natl. Petroleum News*, **22** (x), 46 (1930); Moscicki and Kling, *Przemysl Chem.*, **4**, 2 (1920); *Metan*, **1**, 121 (1917); Wiggins, U.S. Bur. Mines, *Bull.*, **200** (1922); Champion, U.S. 1,943,367—8 (1934).

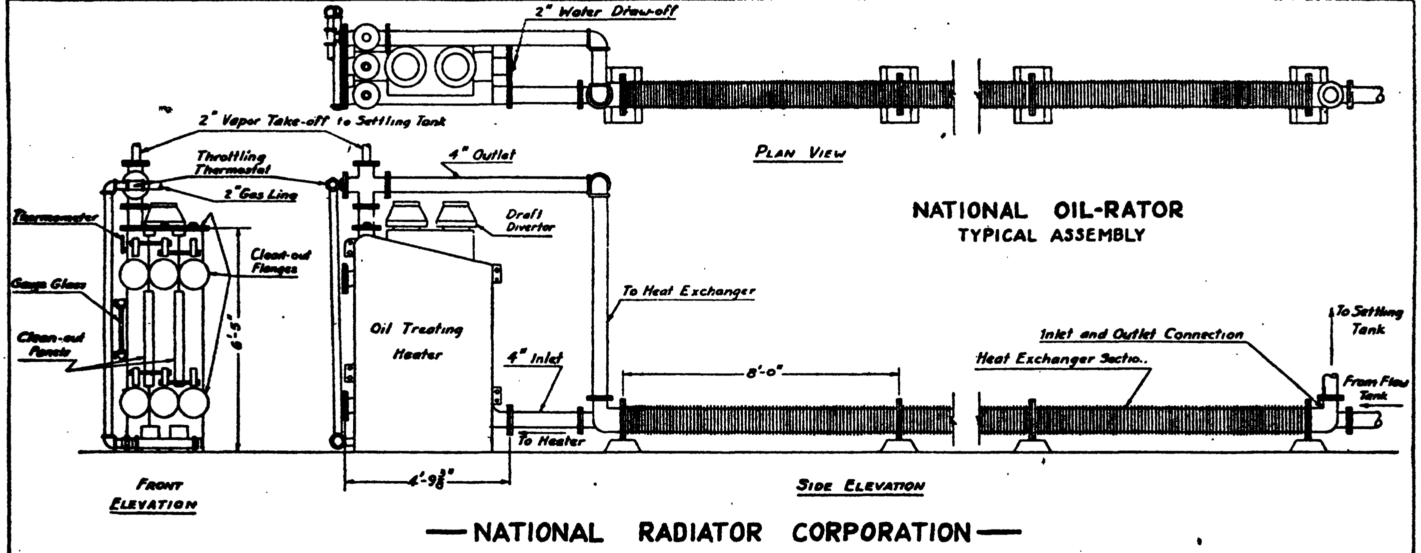
[4] Wadsworth, U.S. Bur. Mines, *Bull.*, **162** (1919); Dubbs, U.S. 1,123,502 (1915).

[5] U.S. 1,928,282 (1933); cf. Collins, U.S. 1,028,439 (1912).

[6] Pollock, U.S. 1,847,413 (1932).

[7] Hyman and Schlandt, U.S. 1,860,248 (1932).

[8] National Radiator Corporation, Johnstown, Pennsylvania. See Novotney and Hunter, U.S. 1,968,614 (1934), and Burck, *Petroleum Z.*, **20**, 1887 (1924).



NATIONAL OIL TREATING HEATER ESSENTIAL DATA

		High Efficiency Heaters				High Capacity Heaters			
Size of Heater		2-E	3-E	4-E	5-E	2-C	3-C	4-C	5-C
Number of Sections		2	3	4	5	2	3	4	5
Capacity – Based on 42 Gals. per Bbl. and 70° Temperature rise –	Bbls. Water per hr.	10.45	20.90	31.35	41.80	18.29	36.58	54.87	73.16
Output	B.T.U. per hr.	256,000	512,000	768,000	1,024,000	448,000	896,000	1,344,000	1,792,000
Efficiency	Percent	80	80	80	80	55	58	55	55
Number of Burners		2	4	6	8	3	6	9	12
Manifold Pressure	Inches of Water	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Heating Value of Gas	B.T.U. per cu. ft.	1100	1100	1100	1100	1100	1100	1100	1100
Gas Required	Cu. ft. per hr.	291	582	873	1164	740	1480	2220	2960
Approximate Shipping Weight	Lbs.	4000	5885	7775	9650	4150	6200	8200	10300

FIG. 84. The National Oil-Rator for the thermal de-emulsification of crude petroleum emulsions.

tapped off at many points into an axial pipe in which the oil-rich liquid is further separated [1]; (2) the emulsion is heated above 100° C. in a closed narrow vessel, a large free space above the emulsion being avoided and the necessary effective pressure being furnished by the vapour tension of the liquid of the emulsion. The emulsion is caused to pass over the sharp edges of a suitable material, *e.g.*, metal turnings so as to flatten out and remove the films of the emulsion and so form large drops[1]; (3) the emulsion is centrifuged against heated plates, whereby the water is immediately evaporated.[2]

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[1] Meurk, U.S. 1,921,689 (1931).

A detailed study of the heating process for crude oils has been made by Egloff and Berkman[3] under the title: "Superheating and Foaming Phenomena in Dehydrating Emulsified Oils." Heating leads to changes in the viscosity and surface tension of the emulsion, to a change in the densities of the phases, and to changes in the colloidal properties of the emulsifying agent. Regarding the last factor, the effect is individual, depending on the nature of the components involved and the physical condition of the system. When the temperature of the emulsion is suitably raised, a change in the state of aggregation occurs and the steam and oil vapours produce breaks in the surrounding protective films.

The authors describe two phenomena commonly observed in heat dehydration: (1) priming or puking of the oil, a superheating effect causing a kind of explosion; (2) foaming of the emulsion. They sum up their investigation thus: "The extent of superheating is determined by the temperature necessary for sustaining equilibrium of the liquid against external pressure. Ebullition is restricted to certain localities in the liquid. A gradation in the effectiveness of the material serving as a nucleus for the superheating phenomenon is observed. The extent to which superheating of a liquid is carried out and the time during which it is held under a superheated condition are the characteristics and the variable in the process. . . . The mechanism of dehydration includes, in addition to the prevention of the superheating influences, the breakdown of foam during the process. Pressure and high temperature favouring dehydration likewise reduce the tendency of the emulsion system to foam. At the same temperature, more water may be separated from an emulsion where a vapour space is present than where no vapour space exists. The lack of vapour space substantially prevents foam formation, thus accounting for changes in the dehydration effect."

The nature of the oil itself decides the intensity and permanence of foaming. Substances, such as gasoline, can exert marked influence on foaming and the evaporation of water. One factor which decides the extent of foaming of emulsified oil is the depth of the oil in the container, foaming increasing with depth and attaining a maximum at a definite temperature. The authors believe that the two phenomena of superheating and foaming indicate the existence of a self-cooling effect, which may be interpreted as a consequence of superheating when the heat from the oil is absorbed more quickly than from an external source. Further, it may be due to a rupturing of the films of emulsifier or, perhaps, to chemical changes taking place in the system and requiring heat to be taken from the system itself with an accompanying cooling effect.

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[1] N. V. Machinerieën-en Apparaten Fabrieken, Fr. 770,268 (1934).

[2] Ger. 273,100 (1909).

[3] *J. Phys. Chem.*, **39**, 265 (1935).

Filtration methods which depend on the preferential wetting of a porous or powdered solid material by oil are sometimes effective in resolving crude oil-field emulsions (see p. 217). Physico-chemical principles of great importance are involved. The " septum " employed may be excelsior,[1] sand,[2] diatomaceous earth, clay or marble,[3] hematite, lepidolite or hornblende,[4] a porous mass of comminuted Al_2O_3, which has been crystallised in an electric furnace,[5] infusorial earth or cloth.[6] Heating may be of advantage.[7] Initial wetting of the filter material with clean petroleum oil is advised.[8] Van Loenen has described various types of apparatus for the treatment with solids.[9]

Several modifications of the simple filtration scheme have been patented. Trumble [10] passes the emulsion through porous diaphragms, which are of progressively greater area, so as to permit the time of separation for the water to be progressively increased. Meinzer [11] mentions the passage of a pulsating stream of emulsion through a mass of granular solid material such as silica or pyrite. The use of increasingly fine layers of solid particles, such as graded sand, is claimed by Pollock.[12] Fisher [13] proposes that the emulsion be passed between two relatively moving bodies such as intermeshed gears, one of which is preferentially wetted by the oil phase of the emulsion and the other by the aqueous phase. Agitation of the emulsion with two different solids each preferentially wetted by one phase is claimed by Meinzer.[14] Thus, the emulsion is agitated by air in the presence of zeolite minerals, and FeS preferentially wetted by oil, and quartz minerals, preferentially wetted by water. A quiescent zone is baffled off in the agitator and the mixed but unemulsified liquids are withdrawn to a settler after filtration. Rollers having preferential wetting qualities have been claimed by Stevens.[15] Other methods include a combination of silica sand and static field,[16] sharp-edged glass particles of 10 to 30 mesh,[17] and the vibratory effects from a rare-gas tube.[18]

Chemical Methods for the de-emulsification of crude petroleum emulsions have found wide application, and present much variety. The essential principle involved is that, when an emulsion of water in oil is stabilised by an oil-soluble (hydrophobe) colloid, the addition of a suitable water-soluble (hydrophile) colloid can bring about coalescence. Academically such a scheme has been made familiar by Clowes[1] in his experiments on antagonistic electrolytes, which we have already discussed (see p. 229).

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[1] Winters and McCamon, U.S. 1,366,143 (1921).

[2] Meredith, U.S. 1,480,091 (1924); Roth, U.S. 1,665,189 (1928); Campbell, U.S. 2,133,186 (1938); Fisher, U.S. 2,018,302 (1935); Robinson, U.S. 1,987,870 (1935).

[3] Eddy, U.S. 1,807,833 (1932); de Groote, U.S. 1,922,154 (1933).

[4] Robinson, U.S. 1,974,692 (1934).

[5] Garrison and van Loenen, U.S. 1,947,709 (1934).

[6] Dyer and Heise, U.S. 1,242,784 (1917); cf. Gifford, U.S. 1,812,629 (1931).

[7] Manley and Knoss, U.S. 1,972,454 (1934).

[8] Zoul, U.S. 1,501,877 (1924); Eddy, U.S. 1,807,833 (1931).

[9] U.S. 1,944,479, 1,944,480, 1,967,601, 1,974,698 (1934); Holmes, U.S. 2,165,703 (1939).

[10] U.S. 1,304,124 (1919); cf. Haseman, U.S. 1,914,665 (1933).

[11] U.S. 1,887,774—5 (1932).

[12] U.S. 1,847,413 (1932).

[13] U.S. 1,932,093 (1933).

[14] U.S. 1,911,839 and 1,911,840 (1933); Brown and Meinzer, U.S. 1,911,797 (1933).

[15] U.S. 2,174,849 (1940); 2,210,782 (1940); 2,217,782 (1940).

[16] Cerf, U.S. 2,030,198 (1936).

[17] Howes, U.S. 2,228,353 (1941).

[18] Mitscherling, U.S. 2,188,269 (1940).

Water-soluble soap is a common agent employed in the chemical treatment of emulsions. Sodium and potassium soaps are soluble in both water and oil, but according to Fischer,[2] the aqueous solutions of these soaps contain hydrated colloid, which is no longer soluble in oil. Sodium oleate is the basis of several patented compounds, *e.g.*, "Tret-o-Lite," which contains 83 per cent. of the oleate, 4 per cent. of phenol and 1 per cent. of water, with sodium silicate, sodium resinate and paraffin.

Matthews and Crosby[3] describe tests made with this mixture; they found that a 1 per cent. aqueous solution of "Tret-o-Lite," added to the emulsion in the ratio of 0·1 to 1·0 per cent by weight, caused separation following upon agitation and subsequent settling; working at a temperature of 65° C., expedited the de-emulsification.[4]

That the phenol constituent is important is the belief of Mead and McCoy,[5] who, however, hazard the opinion that by metathesis there result sodium phenolate and oleic acid soluble in mineral oils and able to attack the emulsion film. It was found that progressively more efficient results follow the use of polyphenols which are successively more and more acidic in character.

Dodd[6] concludes that substances *soluble in both phases* are effective in breaking crude-oil emulsions, provided very small amounts of HCl or H_2SO_4 are also added. The mutually-soluble substances, of which phenol was outstanding, convey the acid through the oil phase to the water globules. Butyric acid (soluble in water and oil) readily breaks the emulsions, as does also refinery acid sludge, *i.e.*, a complex by-product in the sulphuric acid purification of petroleum distillate. In all cases heating at 50° C. assists de-emulsification.

Sometimes the crude-oil emulsions can be "broken" by merely agitating with sodium carbonate. This is due to the formation of sodium soaps (acting as hydrophile colloids) formed by the reaction between the alkali added and the fatty acids present in the oil. The use of sodium salts of sulphonated mineral oils has been patented by Francis and Rogers,[7] who advocate the addition of such agents to the heated emulsions. De-emulsification readily follows such treatment. In this connection it is of interest to note that Levinstein has patented as emulsifying agents, for emulsions of oils, fats and waxes in water, sulphonated stearic acid [1] and sulphonated palmitic acid.[2]

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[1] *J. Phys. Chem.*, **20**, 407 (1916).

[2] *Science*, **43**, 468 (1916). The subject is very clearly outlined in Brit. 180,447 (1921) by Sharples Speciality Co.

[3] *Ind. Eng. Chem.*, **13**, 1015 (1921); cf. Gill, Brit. 180,447 (1921).

[4] Barnickel, U.S. 1,223,659 (1917) and U.S. 1,467,831 (1923). A full discussion of the operation of the "Tret-o-Lite" process is given by Dow, *loc. cit.*, p. 48, and by Cuno, *Chem. Met. Eng.*, **35**, 165 (1928).

[5] *Colloid Symposium Monograph*, **4**, 45 (1926). Cf. Sabato, *Rev. facultad. cienc. quim.*, **14**, 209 (1939).

[6] *Chem. Met. Eng.*, **28**, 249 (1923).

[7] U.S. 1,299,385 (1919); *vide* also Matthews and Crosby, *loc. cit.*, p. 1015.

Of other hydrophile colloids recommended in the de-emulsification of crude oils may be mentioned gelatin (glue) and starch. It is possible to prepare a concentrated gelatin mixture in fuel oil, which readily " breaks " these emulsions. Starch added in suitable oil-soluble form also acts very effectively, although starch is not usually considered a strong protecting colloid for oil-in-water emulsions. In a discussion of the use of these reagents it has been pointed out by Ayres [3] that " nothing of value can be said in regard to the percentages of such hydrophile reagents required to break these emulsions, because, in practice, the effects of the reagents are progressive. Taking, for example, an emulsion which can be separated in a given continuous centrifugal at the rate of five barrels an hour, the addition of 0·001 per cent. of oil-soluble sodium soap, glue, or starch, several hours before centrifuging, will cause the rate of separation to be increased to fifteen barrels an hour. The same increase may be obtained by the addition of 0·01 per cent. of hydrophile colloid thirty minutes before centrifuging, or the addition of 0·1 per cent. at the time of centrifuging. Within practical limits, the more reagent is used the further will coalescence proceed in a given time. An absurdly small percentage of hydrophile colloid is enough to insure complete coalescence by contact if the emulsion is given time to come to equilibrium."

The number of patented chemical reagents for resolving crude-oil emulsions is large (see Appendix). *Whilst a given reagent may be effective for a given emulsion, it may fail with another emulsion.* Addition of the reagent is recommended at the well head or at a junction of several pipe lines leading from wells. Less reagent is required if the emulsion is treated warm. According to Roberts [4] the emulsion may be pumped through a flow-line into which is introduced an inert gas such as CO_2. Water is added and the mixture passed through an homogeniser. A chemical demulser is next added to the emulsion as it travels through the flow-line into a settling tank.

COALESCENCE BY ELECTROLYTES

By adding suitable electrolytes to oil-field emulsions, the charge on the water globules is neutralised and coalescence results. Such a scheme also appertains to emulsions of the oil-in-water type, as was shown by Hatschek.[5] Bottars [6] has patented the use of acids for the separation of oil-in-water emulsions.

Investigations by Sherrick [7] on the adsorption of H ions when acids were added to Texas oil-field emulsions showed that the concentration of hydrogen ions necessary to effect complete discharge of water from the oil ranged around the value 10 × 10^{-1} normal. His method was to place 200 c.c. of emulsion, containing 25 per cent. of water, in a 500 c.c. ground-glass-stoppered graduated flask and add 50 c.c. of acid solution. After being shaken twenty minutes in an electrically-driven shaker, the flask was stood for twenty-two hours, when the percentage of water in the oil layer was determined.

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[1] U.S. 1,176,378 (1916).

[2] U.S. 1,185,213 (1916).

[3] *Ind. Eng. Chem.*, **13**, 1013 (1921). On the question of de-emulsifying efficiency, see table given by Lottermöser and Calantar, *Kolloid-Z.*, **48**, 365 (1929).

[4] U.S. 1,802,090 (1931). See Kuczynski, *Petroleum Z.*, **24**, 398 (1928).

[5] *Kolloid-Z.*, **9**, 159 (1911).

[6] Norwegian, 26,667 (1916).

[7] *Ind. Eng. Chem.*, **13**, 137 (1920).

The order of efficiency of the acids was $HCl > H_2SO_4 >$ acetic.

Much better results were obtained by Sherrick, using ferric chloride solutions, from which ferric ion adsorption took place, resulting in separation of the emulsion. The $FeCl_3$ solution contained 66·24 grms. $FeCl_3$ per 100 c.c. To 200 c.c. of emulsion were added this solution and water, and the mixture shaken as before. It was found that with low concentrations of ferric ion the de-emulsification was perfectly regular ; with higher concentrations, however, there was not a separation of the water phase itself, but jellies of varying stability resulted. It was found that these jellies contained positively-charged particles, the adsorption of ferric ions having carried the particles past the iso-electric point.[1] It was found that a saturated solution of sodium nitrate immediately destroyed the jellies, owing to the strong adsorption of the NO_3 ion. It followed from this that a solution of ferric nitrate should precipitate the original emulsion without intermediate jelly formation, since the adsorption of ferric ion would counteract to a certain extent the effect of the NO_3 ion. By the simultaneous adsorption of ferric and nitrate ions on the emulsion a spongy mass separated out, but this was very mobile and easily broken. Sherrick concludes that these results " clearly show that both ions have an effect on the precipitation."

Dodd[2] has repeated Sherrick's work, using an emulsion from the Midway-Sunset field of California. The water globules were negatively charged. On trying the effect of acids, the order of efficiency was the reverse found in Sherrick's experiments, and acetic acid proved the most efficient. Again, ferric chloride and ferric nitrate solutions did not break the emulsion, but merely mixed into it. Partial breaking followed the addition of ferric sulphate or $CaCl_2$ after long heat-treatment. Dodd concluded that " on the whole the action of electrolytes alone, on Californian emulsions, was not sufficient to encourage further investigation."

It is interesting to note that occasionally oil-in-water petroleum emulsions are encountered, and addition of salts with a polyvalent cation, *e.g.*, $CaCl_2$ and $AlCl_3$, serves to break them. Van der Minne mentions an instance of such emulsions which are commercially resolved by the aid of sea-water.

Electrical Methods are based on the fact that coalescence of the water globules may follow the passage of an electric current (direct or alternating) through the emulsion. High potential alternating current is usually employed. F. G. Cottrell took out the pioneer patent[3] in this connection, claiming that the water particles " are subject to electrostatic forces dependent upon the relative potentials and dielectric constants of the materials in contact and caused to coalesce into masses " easily removed by settling or centrifuging. Braley[1] mentions that emulsions holding even 65 per cent. water have been economically dehydrated to 0·5 per cent. water and refuse by this process.

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[1] Cf. Ellis, *Z. physik. Chem.*, **89**, 145 (1914).

[2] *Chem. Met. Eng.*, **28**, 249 (1923).

[3] U.S. 287,115 (1911).

The " electrical dehydration " process has been described by W. G. and H. C. Eddy.[2] A galvanised steel tank (the " electrical treater "), approximately 3 feet in diameter and 8 feet deep, is provided in the centre with a vertical shaft carrying a number of circular discs. The shaft is mounted on an insulated bearing and slowly rotated. The tank shell is earthed and acts as one electrode ; the shaft acts as a revolving electrode, and a potential difference of 11,000 volts (alternating current and of any commercial frequency) is maintained. The oil-field emulsion is fed continuously into and through the annular electrical field so produced between the tank shell and the disc edges, whereby de-emulsification ensues. The freed oil and water pass into a settling tank, where separation is completed into oil and water (containing dissolved salts). A plant operated from a single circuit and motor may consist of any number of treaters from 1 to 8 in even multiples, also in banks of 6 units each. The capacity per treater averages from 300 to 1,000 barrels of oil per day, the character of the emulsion being an important factor in this respect. The consumption of electrical power ranges from 5 to 75 watt-hours per barrel of dehydrated oil the average cost of electricity (1921) being 1 cent. per 20 to 25 barrels. Where possible the plant is located so as to secure a gravity flow from the supply tank through the treaters and trap to the shipping tanks, requiring a minimum of piping and pumps.

The maximum efficiency depends upon an optimum working temperature. The average temperature maintained is 57° C., but particularly stable emulsions may have to be raised to about 82° C. before treating electrically. With oils containing volatile constituents, an enclosed type of heater becomes necessary. An extension of this method has been made by McKibben,[3] who proposes to pass the emulsion, heated to produce the vaporisation of the water, through an intensified electric field. The vapours are condensed and cooled, and the water separated off.

The theory underlying the Cottrell process and its modifications is that the emulsion serves as a multitude of electrical condensers, the electrodes or poles being the water globules and the continuous oil phase serving as the dielectric. Under the influence of a high-potential alternating field the charged water particles rupture the enveloping oil films and coalesce, forming larger drops. According to W. G. and H. C. Eddy,[4] who followed such a test by the aid of the photomicrographic cinema film, " this action of stress and strain, attraction and repulsion on the conducting water particles continues until all the microscopic drops of water in the original emulsion have broken the bonds of the entrapping oil films, the larger droplets serving as nuclei until the entire water content is freed into large drops which readily settle out."

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[1] *Trans. Am. Electrochem. Soc.*, **35**, 209 (1919).
[2] *Ind. Eng. Chem.*, **13**, 1016 (1921).
[3] U.S. 1,299,590 (1919).
[4] *Ind. Eng. Chem.*, **13**, 1016 (1921).

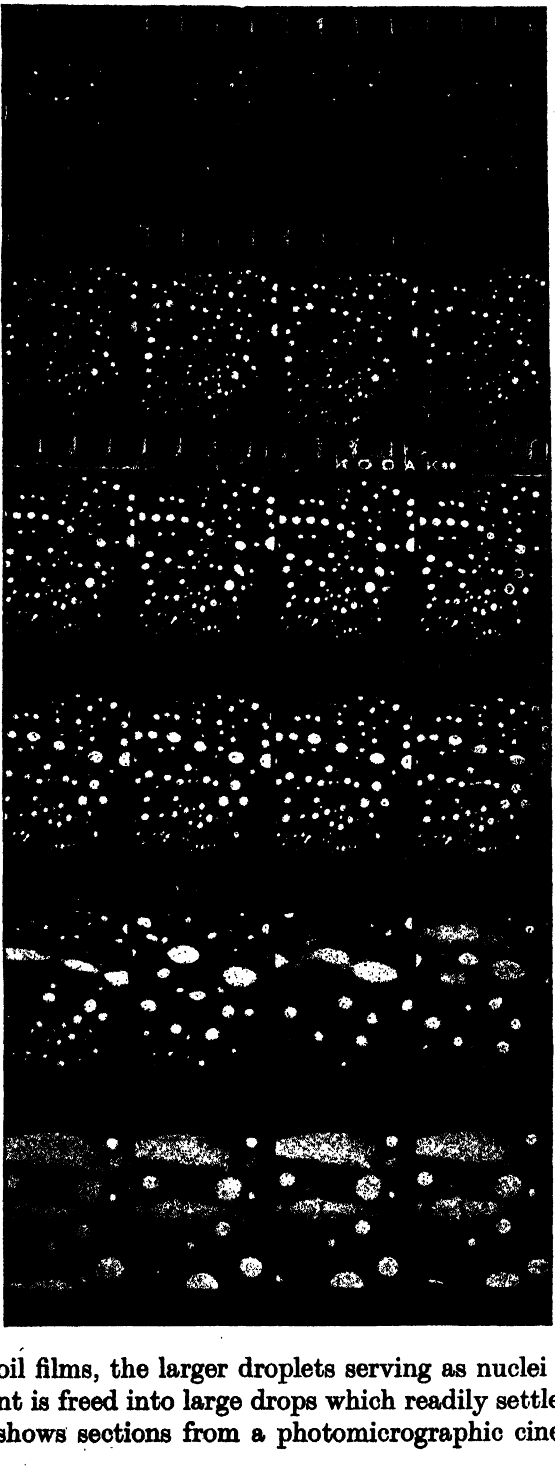

FIG. 85. Photomicrographic cinema record of the "Cottrell" electric dehydrating process. (Eddy and Eddy.)

Fig. 85 shows sections from a photomicrographic cinema film (made by W. G. and H. C. Eddy) taken four per second and magnified fifty times. Each section contains four individual pictures. The first section shows the untreated emulsion, with 35 per cent. water as internal phase. The succeeding sections show the continued coalescence into a few large drops of the water globules under the influence of the electric current. The change can be clearly followed from one section to the next; particularly noticeable is the chain started from the larger water globules that happened to be somewhat lined up in the crude emulsion. The large water drops, as shown in the completed section, are now in a condition to settle freely to the bottom by gravity, and clear water can be automatically drawn off in a continuous stream.

Starzewski,[1] working with natural brine crude-oil emulsions, finds that breakdowns are the more numerous the shorter the distance between the electrodes, the higher the tension on the electrodes and the higher the temperature of the emulsion. Pawlikowski[2] dispersed H_2SO_4 in crude oil and studied their resolution under the influence of a 50-cycle A.C. up to 17,000 volts. He confirmed Cottrell's theory. Inequality of the electric field causes a rapid coagulation of aqueous globules, which are drawn into places where the lines of electric field are most dense. Coagulation is a function of the P.D., since a secondary *dispersion* of the coagulated phase may occur at the electrodes on sufficiently increasing the P.D.

An important study of the action of electric fields on W/O and O/W emulsions has been made by Kuczynski.[3] Using the microscope, he observed that the globules of the emulsions are deformed in the electric field and arrange themselves in chains parallel to the lines of force. With W/O emulsions coagulation occurs when the globules of a chain make contact. In consequence, the chains conduct the current and exhibit a characteristic mutual repulsion. (With W/O emulsions these chains do not coagulate.) Qualitatively studying the conditions of chain formation, Kuczynski observed that under the influence of the electric field, concentration changes occur in the sense that the water globules congregate in the zones of the strongest field but with O/W systems, the oil globules congregate in places of weakest field. In charging a condenser with emulsion, energy is used not only for polarising the dielectric medium, but also for mechanical work, namely, for deformation of the droplets and for changes of concentration.

A detailed theoretical examination of the formation of chains has been given by Krasny-Ergen,[4] whilst Hassler has a patent for preventing chains.[5]

A development in electrical dehydration is the *Cage process*. Only one electrode is employed, impressing a high-tension charge of alternating sign on the emulsion. Charges of 100,000—200,000 volts are applied.[6]

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[1] *Przemysl Chem.*, **14**, 97 (1930).

[2] *Ibid.*, **12**, 501 (1928).

[3] *Ibid.*, **13**, 137, 161 (1929).

[4] *Ann. Physik.*, **27**, 459 (1936).

[5] U.S. 2,045,465 (1936).

[6] Wilcox, *Oil and Gas J.*, **28**, No. 33, p. 38 (1930). See *Petroleum Times*, **22**, 393 (1929).

De Brey[1] treats the emulsions with a pulsating alternating current having a peak voltage which is a multiple of the effective voltage. In this way it is possible to retain the greater activity of high potentials, while the total electric energy remains lower, since the period during which the high potential operates is decreased. Van der Minne[2] describes the process, thus :—

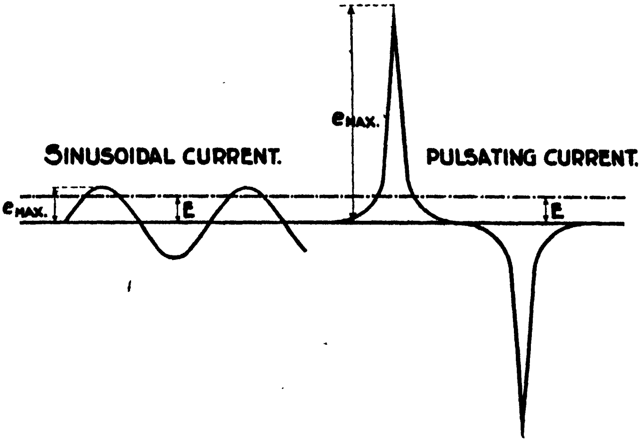

FIG. 86.

" Fig. 86 illustrates an ordinary sinusoidal current and a pulsating current of this kind, the effective top tension being 5–10 times as much as that of a sinus current of the same energy. The action may be visualised in this way :—

" The brief top of high potential is sufficient to charge the water drops by induction, the coagulating effect of these charges being the same as if this high potential had lasted longer, while the loss due to electric conduction is considerably less. It is for emulsions rich in water and those which show a marked tendency towards chain formation that less consumption of electric power is of particular importance.

" Under working conditions, the process is as follows : The more or less heated emulsion is made to pass one or more apparatus with progressive voltages. In these apparatus the emulsion flows along a slowly revolving electrode, while the wall of the apparatus forms the other electrode. The top tension may sometimes reach 40,000 volts. The result is that the emulsion is coarsened. Finally, this coarse emulsion is allowed time to settle in settling tanks and to give off a layer of water in the same way as in chemical separation."

The use of direct current has been patented by Siebert and Brady.[3] The method is based on the principles of cataphoresis, but with oil having a low dielectric constant, cataphoresis is not so pronounced as the electrostatic effect. A voltage of 250 to 600 volts is employed, and the current varies from a few milliamps. to 10 amps. This process, however, finds only a very limited application, though the Gulf Production Company embody it in their "combined method" for dehydrating oils in the Goose Creek (Texas). They employ a combination of closed heating, settling, direct-current electrical treatment, and centrifuging. The evaporation loss is very small, and the fuel consumption low. McKibben[1] has devised a process wherein a continuous, uninterrupted, uniform electric field is maintained between electrodes with a conduit constituting a relatively long path, to polarise the water globules tending to chain formation, and the emulsion is passed through the field slowly enough to break up or prevent persistence of chains of polarised globules of entrapped water between the electrodes. Separation into oil and water is thus effected. A very similar idea underlies a patent by Harris.[2] Electrodes in the emulsion are caused to approach each other sufficiently to lead to formation of water chains between the electrodes, through which heavy short-circuit currents can flow. The electrodes are then separated and the current interrupted, whereupon water settles out.

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[1] Dutch 14,082 (1926) ; U.S. 1,570,209 (1924).

[2] *Proc. World Petroleum Congr.* (London, 1933), 1, 516 (1934).

[3] U.S. 1,290,369 (1919).

According to Roberts[3] crude-oil emulsions may be resolved by the combined action of magnetic and electrical fields. Again,[4] the emulsion may be subjected to the repeated action of magnetism of different frequencies, each of which frequencies is adapted for one component of the emulsion. Herbsman[5] claims treatment with violet and ultra-violet rays, X-rays, cathode rays, canal rays or radiation from radio-active substances.

CONDENSER WATER EMULSIONS

An important engineering problem has arisen in connection, more particularly, with forced lubrication in steam turbines. When steam passes through the valve chest and cylinder of an engine, particles of lubricating oil are carried along in a state of very fine subdivision, so fine, in fact, as to lead to the formation of emulsified oil when the stream is condensed. Condensed water, in such cases, is milky, and the entrapped oil is present as an exceptionally stable emulsion, the oil particles being from 0·0006—0·00006 cm. diameter and negatively charged. Philip[6] has pointed out that mineral oils will emulsify in distilled water to a low concentration, but not in the presence of electrolytes, and we have already noted that the emulsifying capacity of mineral oils has to be determined before their suitability for lubricating purposes can be definitely established.

Oily condensed steam is an unsuitable feed for high-pressure boilers, as a thin coating of oil on the heating surface causes intense heating of the plate, and the trouble is cumulative. A layer of oil 1/50 inch thick in a boiler working at 150 lb. per square inch pressure will increase the wall temperature by 350° C.

Condenser water emulsions are of great interest, inasmuch as mechanical, chemical and electrical methods have been used for separating the oil, owing to the value of the distilled water for boiler feeding and other purposes demanding chemically pure water.[1]

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[1] U.S. 1,299,589 (1919); 1,304,786 (1919).

[2] U.S. 1,281,952 (1918); cf. also Laird and Raney, U.S. 1,116,299 (1914), 1,142,760 (1915) and 1,142,761 (1915).

[3] U.S. 1,949,660 (1934).

[4] Roberts, U.S. 1,978,509 (1934).

[5] Brit. 356,926 (1930); U.S. 1,783,471 (1930); Ger. 592,877 (1934).

[6] *J. Soc. Chem. Ind.*, **34**, 697 (1915).

Under the mechanical methods prior mention must be made of Hatschek's scheme.[2] In this it is proposed to coat the filtering surface of any suitable type of filter (*e.g.*, filter press) with a layer of calcium carbonate[3] of thickness depending on the rate of filtration per unit filtering surface, the percentage of emulsified oil, and the pressure used in filtering. Clear water passes through such a filter, the oil being retained on the surface of the chalk layer. Undoubtedly the main factor operating in this filtration is not the size of the pores, but the fact that water wets calcium carbonate more readily than does oil.[4] Emulsions of the water-in-oil type can be repeated in a similar manner, viz., by passing the emulsion through a filter which is more easily wetted by oil than by water. Thus, when a crude petroleum oil-field emulsion is passed through powdered vulcanised rubber or iron sulphide, clear oil passes through, the water being retained at the filtering surface.

Of late, attention has been paid to the removal of oil from steam condensate by means of active carbon.[5] The following account is reproduced by permission : [6] " It was found that the high-grade granular Hydraffin T active carbons were very effective for this purpose. These carbons would be regenerated, when charged with oil, by extraction with organic solvents, but it was considered that this would not be an economic proposition. A cheap grade of carbon was required which was specially suitable for adsorbing oil, and which could be thrown away or burnt after use. Hydraffin K. 87 (special), manufactured by the Carbo-Norit Union, was found to meet these requirements.

"Exhaustive large-scale experiments were carried out at the Mainkur works of the I. G. Farbenindustrie A.-G. Ordinary condensed steam from the works was first passed through a mechanical oil separator, which left about 3·5 mg. of oil per litre in the water. The water was then filtered through a bed of fresh carbon about 1 m. (39 in.) thick. The amount of oil in the filtrate was at first *nil*, but subsequently rose very slowly during the test period, which extended over several weeks. When the filtrate was found to contain about 1 mg. of oil per litre, the used carbon was tested, and was found to have taken up 15 per cent. of its own weight of oil : 1 kg. of carbon had, therefore, removed 150 grm. of oil from 60 cub. m. of water (= 13,200 gallons).

" The final result proved to be just as good when the original condensed steam contained a larger quantity of oil, but for the sake of economy it was considered advisable to employ preliminary mechanical separation when the steam condensate contained large amounts of oil.

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[1] General accounts are given by Glaser, *Feuerungstechnick*, **8**, 149 (1920) ; Splittgerber, *Wasser*, **5**, 146 (1931) ; Schöne, *Braunkohle*, **31**, 61, 82 (1932) ; Schiuman, *Power Plant Eng.*, **36**, 770 (1932) ; Mott-Smith, *Repts. Hawaiian Sugar Tech.*, **7**, 27 (1941). The removal of water from transformer oil is discussed by Ketnath, *Elektrotech. Z.*, **54**, 1259 (1933).

[2] *J. Soc. Chem. Ind.*, **29**, 125 (1910).

[3] Brit. 26,228 (1908) ; cf. Trumble, U.S. 1,304,124 (1919).

[4] This principle is used by Robinson and Parks, Brit. 268,547 (1926).

[5] Jaenicke, *Chem. Ztg.*, **56**, 630 (1932) ; cf. *Chem. Age* (London), **27**, 204 (1932), and Netuka, *Chem. Obzor.*, **7**, 257 (1932).

[6] *Ind. Chemist*, **7**, 452 (1931).

"The water obtained by filtration through this carbon was bright, clear and free from smell and taste. The loss of heat during filtration and the pressure drop due to the resistance of the carbon bed were found to be negligible.

"The apparatus can be constructed very simply, consisting of a cylindrical container of, say, 1 m. diameter, in which a bed of the carbon, 1 m. thick, is supported between two sieves. The water passes through this filter at a speed of 6 to 16 in. per minute, depending on conditions. It was found that a carbon filter of these dimensions will treat about 2,200 gallons of oil-contaminated water per hour, and the cost of the process works out to between ½*d.* and 1*d.* per 1,000 gallons. The carbon was supplied in a moist state, containing about 50 per cent. of its own weight of water, but the price (£33 per ton) was calculated on a 10 per cent. water content."

CHEMICAL DE-OILING

Although filtration of oily water through carbon, cloth or filter-earth [1] may prove effective, the addition of chemicals to form gelatinous precipitates which adsorb oil is quite common practice. Advantage is taken of the fact that the oil globules are negatively charged, and can therefore be caused to coalesce by addition of a suitable electrolyte with a cation of high valency.

Commercial sulphate of alumina is most commonly employed. The salt contains on the average 53 per cent. of $Al_2(SO_4)_3$, equivalent to 16 per cent. Al_2O_3. The reagent is run into the condensed water together with sodium carbonate or caustic soda, whereupon a gelatinous precipitate of $Al_2O_3 \times (H_2O)_n$ is formed, which unites with the oil globules so that these now become easily filtered. Careful regulation of the alkali is required to avoid redissolving the precipitate.

Controlled mixing of the reagents is essential and the mixture is then filtered through wood fibre and then quartz sand. As installed by the Paterson Engineering Co., Ltd., at Summer Lane Generating Station, Birmingham, this method deals with a peak load of 800,000 lbs. of condensed steam per hour, at a cost for aluminium sulphate and soda ash of only 0·169*d.* per 1,000 gallons treated.[2]

Bartmann,[3] dealing with the removal of oil from steam accumulators, mentions that aluminium sulphate and soda ash are added to the water, and that it is necessary to blow down when the sludge contains 40 per cent. of oil. According to Beal and Stevens,[4] it is better to use alum and sodium aluminate. "By using a slight excess of sodium aluminate in the treated condensate, and a slight hydroxide alkalinity, a suitable type of boiler feed water free from oil pollution is produced."

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[1] See Johnson, *Repts. Assocn. Hawaiian Sugar Tech.*, *12th Ann. Meeting*, **1933**, 105. Stein, *Chem. App.*, **19**, 133 (1932), deals with the separation of emulsions on filtration through filter cloth. A patent by the Metcalfe-Shaw Corpn., Brit. 179,194 (1922) deals explicitly with the use of porous materials, such as an endless moving belt of cotton which dips into the emulsion at one point and is squeezed between two pulleys at another point.

[2] "The Purification of Industrial Water," The Paterson Engineering Co. Ltd. (London).

[3] *Arch. Warmewirt.*, **10**, 415 (1929). See Main, *Steam Eng.*, **1**, 334 (1932). Jungwirt, *Chem. App.*, **14**, 194 (1927), describes Dijxhoorn's method of filtration through a bed of aluminium hydroxide, Dutch 14,335 (1926).

[4] *J. Soc. Chem. Ind.*, **50**, 313 T. (1931).

It is of interest to note that Woods[1] solved the oil waste problem of a large machine shop by using aluminium sulphate. A soluble cutting fluid containing an emulsifying agent was used to cool tools, and this interfered with the operation of a sewage-disposal plant. Aluminium sulphate broke the emulsion, and lime was used to maintain the *p*H at 6—8. Filtration through sand followed.

Stutson[2] cleans boiler condensate containing 30 parts per million of emulsified oil by addition of ferric sulphate at *p*H between 5·5 and 8·6, thereafter filtering.

According to Hatta,[3] the addition of $Fe(OH)_3$ with subsequent filtration through sand or coke is very effective. Thus 1 ton of water containing about 0·005 per cent. of oil requires 12 grm. $FeCl_3$ and 6 grm. of NaOH. The use of coke and Terry cloth filters is discussed by Walden,[4] whilst Joos,[5] in a general description of methods, refers to chilling and subsequent filtration through cloth or paper.

Other types of industrial emulsions are separated by the use of electrolytes, *e.g.*, HCl, H_2SO_4, $AlCl_3$, $BaCl_2$, etc., the important factor being the concentration of electrolyte.

The demulsification of oil-contaminated ballast water may be effected by introducing a chemical demulsifying agent and a gas which carries over the oil globules in a foam.[6]

ELECTRICAL DE-OILING

The various electrical systems in use for "de-oiling" condensed waters operate either on the principles of cataphoresis or a combined electrochemical scheme. Typical of the former is the method proposed by Dijxhoorn,[7] who subjects the emulsion to a P.D. of 110 volts as it passes through the feed water-pipe. The Davis-Perrett[8] process is an excellent example of "de-oiling" by electrochemical methods. The condensed water is sent in a zigzag path between iron or steel electrodes arranged in a wooden tank, and an electrical current is passed. Iron is precipitated from the anode and entangles the oil globules, which coalesce to form rusty-coloured flakes. These are easily removed by a filter, leaving clear water practically chemically pure. By suitably arranging the electrodes, the latest plants can operate so that only 0·1 of a B.T.U. (100 watts) are required to treat 1,000 gallons of condensed steam. The plant is simple, only a short time is taken in treatment, and the condensed steam may be treated at as high a temperature as desired.

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[1] *Munic. Sanitation*, **1**, 397 (1930).

[2] *Power*, **79**, 582 (1935).

[3] Japan 41,579 (1922).

[4] *Power Plant Eng.*, **28**, 594 (1924).

[5] *Ibid.*, **28**, 1244 (1924).

[6] Woelflin, U.S. 2,047,989 (1936).

[7] *Le Papier*, **22**, 53 (1919); cf. Fanto and Stritar, *J. prakt. Chem.*, **81**, 564 (1910).

[8] U.S. 783,107 (1905); Brit. 10,874 (1902), 8,175 (1903), 26,577 (1908). Electrolytic de-oiling of industrial effluents is described by Wi, *Ölmart*, **11**, 243 (1929) and Winkelmann, *Chem.-tech. Rundschau*, **44**, 82 (1929).

Paul[1] mentions a milky emulsion of condensed steam containing 3·64 grains of oil per gallon. After the electro-chemical treatment it was quite clear. Analysis of the oily deposit gave: hydrated ferric oxide = 43·58 per cent., oil = 54·52 per cent., water = 1·6 per cent. The ferric hydrate has in this instance entangled about one and a quarter times its weight of oil, corresponding to two and a half times the weight of iron electrically dissolved from the anode.[2]

Another method of electrically de-oiling is to have the condensed water heated in a wooden tank together with enough raw water to make conducting. On passing current between iron electrodes the oil accumulates at the anode. On reversal of the current, the oil floats to the top. The alternations are repeated at intervals. From 0·15 to 0·20 kilowatt will be required per 1 ton of water so treated.

Râscanu[3] has investigated the optimum conditions for the electrical de-oiling of condensate. Laboratory tests were conducted on a mixture of condensate and raw water in beakers with Fe electrodes 210 mm. long (immersed to a depth of 180 mm.) and 110 mm. wide. It was observed that the electric current caused formation of iron hydroxide which adsorbs all the oil. The optimum temperature was 40°–50° C., because the iron is more rapidly oxidised and the time needed to obtain sufficiently clear water is reduced. The optimum time was observed as 25 minutes (for treating 800 c.c.). The amount of residual oil diminished according to the current density, but no proportionality was noted between the two, 20 to 30 milliamps. giving satisfactory results. Too high a current density leads to the excessive formation of iron hydroxide, and this overloads the filter. Aluminium electrodes were tried out but were not recommended. A large-scale installation was built to treat 5 cubic metres per hour by means of 640 Fe electrodes, 20 mm. in diameter and immersed to a depth of 920 mm., with a current of 7·2 amps. and an iron consumption of 2·6 kg. (0·15 per cent. on the weight of the electrodes) per month.

WATER-GAS TAR EMULSIONS

An interesting account of the incidence and problems of water-gas tar emulsions has been presented by Odell,[4] based on an investigation suggested by the Illinois Gas Association. The emulsion is of the water-in-oil type and may contain up to 85 per cent. of water, the greater the water content, the more viscous being the emulsion. The stability of the emulsions is related to the fineness of the dispersion of the water drops.

According to Odell :—

" In the manufacture of carbureted water gas the only fuel used directly other than the generator coke is the carbureting oil. As the substances of which tar is composed are driven from the coal in coking, the source of water-gas is primarily the carbureting oil. In the water-gas process the aim is to convert as much of the oil as possible into a fixed gas with an average heating value high enough to carburet the blue gas. This conversion is never 100 per cent. complete, because appreciable amounts of carbon and of condensable tarry matter always form. The latter on condensing is known as water-gas tar; it may be composed entirely of substances formed by the cracking of the oil or it may contain an appreciable amount of some of the original constituents of the oil. It is not uniform in character and quality; rather the product of one plant is frequently altogether different from that of another plant. The reason for these differences is that the operating conditions, oil used, gas standard, etc., are not the same in all plants.

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[1] " Boiler Chemistry and Feed Water Supplies " (London).

[2] Cf. Goodwin and Ellis, *Chem. Zeit.*, **81**, 724 (1910).

[3] *Ann. sci. univ. Jassy*, **15**, 71 (1928).

[4] U.S. Bur. Mines, *Tech. Paper*, **304**, pp. 49 (1923). See also Morgan and Stolzenbach, *Am. Gas. Assocn. Monthly*, **16**, 245, 277 (1934); Dashiell, *ibid.*, **17**, 426 (1935); Parke, *Am. Gas. J.*, **142** (vi), 32; 60 (1935).

"The tar may be brown, thin, or watery, contain a large percentage of light oils, and have a specific gravity but little greater than 1·00; or it may be black liquid, of molasses-like consistence, containing a much smaller percentage of light oil and having a specific gravity of 1·15 or more. Again, a water-gas tar may contain little or much free carbon and naphthalene."

The gas leaves the superheater at a high temperature (650° to 760° C.), to be reduced suddenly to about 150° C. Most plants employ a water seal or wash box immediately following the superheater, and here some of the tar and water condense and are removed in the wash-box water. The gas still retains tar, and the progressive cooling throughout the system leads to the formation of emulsions; the relief holder, scrubbers and condensers all contain emulsions.

The emulsifying agent responsible for the dispersion of the water in the tar is mainly carbon. However, the most stable emulsions also contain paraffins (sulphonation residue). The carbon, technically known as "free carbon," is not pure carbon, but a hydrocarbon (insoluble in benzene) with a high carbon content. Filtration of the tar to remove free carbon reduces the tendency to emulsification.

Odell found that the nature of the constituents of the tar determined the obstinancy of the emulsions, when the free carbon content remained constant. The emulsion tendency increases as the percentage of uncracked oil in the tar increases. "Naphthalene, naphthalene compounds, and other unsaturated high-boiling compounds of like nature obtained by distilling water-gas tar are not as readily held in stable emulsions containing a high percentage of water, by the presence of free carbon, as are the paraffin oils."

In the laboratory preparation of water-in-oil emulsions, Odell observed that there is an optimum content of carbon, using carbon black as emulsifier. The table on p. 426 is given by Odell in illustration.

"As the amount of carbon was increased to 5·7 per cent. of the oil used, the droplets of water seemed to become smaller and the emulsion was more stable. Seemingly, there is an optimum amount of carbon that should be used to prepare the most stable emulsion; for this particular oil the amount is between 5·7 and 12 per cent. of the oil used. For paraffin oils the amount of carbon required to make stable

TABLE 52

EFFECT OF DIFFERENT AMOUNTS OF CARBON BLACK ON THE FORMATION OF STABLE EMULSIONS OF MOTOR FUEL AND WATER

No.	Volume of Water used, c.c.	Volume of Oil used, c.c.	Total Volume, c.c.	Weight of Carbon Black used, grams.	Carbon Black. Per cent. of Total.	Carbon Black. Per cent. based on Oil present.	Character of Emulsion formed.
1	70	30	100	0·15	0·15	0·6	Very weak; unstable. Large droplets of water.
2	70	30	100	0·60	0·62	2·3	Weak. Droplets of dispersed water smaller than in 1.
3	70	30	100	1·50	1·53	5·7	Fair. Thin fluid.
4	70	30	100	3·00	3·02	11·3	Fair. Water droplets small. Fairly stable.
5	70	30	100	3·60	3·60	13·6	More viscous than in 4. Water separated. Optimum passed.
6	70	30	100	4·20	4·17	15·9	More viscous than in 5. Additional amount of water separated.
7	70	30	100	5·10	5·02	19·3	Very thick. Much water separated.
8	70	30	100	6·00	5·86	22·7	Pasty mass. Most of the water separated.
9	70	30	100	7·50	7·21	28·4	Putty-like mass. Practically all the water separated instantly.

emulsions is less and the optimum amount of carbon is considerably smaller."

Although dehydration of tar by high-tension electric fields does not seem practicable,[1] separation in a Sharples super-centrifuge has been successful.[2] Usually, however, dehydration is attained by heat.[3] Wagner [4] employs a combination of heat, baffling and gravity. Kleinman[5] circulates the tar in a closed circuit through a separate heater and discharges it as a spray into a vertical settling tank. De-emulsification is assisted by reduction of pressure and evaporation of water and light oils. According to Bismarckhütte,[6] water is separated from tar by projecting the emulsion upwardly against a separating surface to which the water adheres and from which it is collected. Electrolytes may be added before heating.[7] Johnson [8] mixes a carboxy acid, *e.g.*, oleic, which is substantially insoluble in water but is soluble in the tar constituent of the emulsion and allows the emulsion to stand at 60°–70° C. to separate water.

The use of alkali under pressure [9] may be combined with the cascade effect of water-attractive solids, such as gravel.[10] An interesting electrochemical (anodic) separation has been described by Simek and Ludmila.[11]

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[1] Steere, *Am. Gas Assocn. Monthly*, **1**, 193 (1919).
[2] Watnabe, *J. Fuel. Soc. Japan*, **8**, 1309 (1929).
[3] Warner, *Am. Gas. Assocn. Monthly*, **4**, 437 (1922); Hanschildt, *ibid.*, **4**, 181 (1922); Kleinman, *Gas Age-Record*, **63**, 349, 353 (1929).
[4] U.S. 1,781,257 (1930).
[5] U.S. 1,847,654 (1932).
[6] Brit. 163,011 (1921).
[7] Marko, Hungarian 99,202 (1929).
[8] U.S. 1,689,728 (1928). Cf. Robinson and Parkes, U.S. 1,696,057 (1928).
[9] Pearson, U.S. 2,185,710 (1940).
[10] Alexander, U.S. 2,168,309 (1939).
[11] *Chem. Listy*, **30**, 298 (1936).

WOOL SCOURING WASTES

A particularly polluting waste is the effluent from wool washing, containing emulsified wool fat (lanolin), soap residues, free fatty acids, higher alcohols, dirt, bacteria and proteins. The amount of wool grease present varies from 0·5 to 3 per cent. The alkalinity of the effluent varies widely and may attain $pH = 11$.

Recovery of the wool fat may be effected by several methods,[1] the simplest being " cracking " by acid, but in this case only partial purification of the effluent is secured. Partial recovery by centrifuging is sometimes practised. Solvent extraction is expensive. Two main technical operations are now common : (1) coagulation with an electrolyte, and (2) a froth treatment.[2]

De Raeve [3] has described a successful method of chlorination. The effluent is heated to 70°–80° C. and 1 lb. of fresh slaked lime in 1 gallon of water is added per 100 gallons of wool scour. Filtration follows with a vacuum continuous filter, and the filtrate is quietly cooled to below 25° C. Chlorine is now injected, when a thick, white grease-rich foam is the result. Addition of sulphuric acid to the chlorinated water liberates the fat, leaving the residual water clear and yellow, containing 0·25–1 grm. of acid per litre. Such fat on the surface is the best lanolin.

The fatty foam is mixed with acidulated water and contains much dirt and " a fibrous substance like tow, which is the gelatinous element oxidised by hypochlorous acid." By filtering through a hot filter-press a grease is obtained, which is a pale yellow from good fleece, but is darker from the pieces. The fat is washed with hot water containing $NaHSO_3$ or SO_2.

Kolsky [4] has proposed coagulation of wool fat in the scour by means of aluminium sulphite. Snell [5] investigated the coagulation with aluminium sulphate and obtained satisfactory results. The sludge contained lanolin mixed with aluminium hydroxide, the latter being removed by hot dilute sulphuric acid.

Several patents deal with the formation of a foam on the surface of the wool scour and its breaking by heat. The following account [6] of the process in use at the works of Cirolanum Ltd. (Gomersal Mills, near Leeds) deals with the application of a special aerating device, the Barber jet.

The effluent is first cleared of wool fibres and coarse dirt by passage through wool-catchers, and is then pumped to the Barber jet machine. Fig. 87 illustrates this jet. It consists of two concentric tubes, 1 and 2, fitting closely enough to permit only a very thin film of liquid to pass through the annulus between, to which it is admitted *viâ* the chamber C from the inlet Y. At the same time, air under pressure is admitted through the inlet X to the chamber B, and so to the inside of the inner tube D, which is perforated with a number of tangentially-directed orifices. The action is as follows: The suspension of grease in water in a thin film travelling at a high velocity occupies the annulus, while fine jets of air are forced into this film, creating an intimate mixture of grease, water and air, tending to coalesce the particles of grease and so separate it from the water phase. The emergent film, which is not ruptured by the air jets, is forced to impinge upon an abutment below the jet boxes. It is found that under this treatment most colloidal materials coagulate to give agglomerate masses. The partially-separated grease and water undergo repeated treatments, and substantial separation is obtained after the fifth.

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[1] Palmer, *Trans. Am. Inst. Chem. Eng.*, **12**, 113 (1919); King, *Textile Manfr.*, **56**, 458 (1930); Smith, *ibid.*, **56**, 452, 458 (1930); Rindl, *S. African J. Ind.*, **6**, 204, 336 (1923); Willard, *Rev. gen. mat. color*, **43**, 427 (1939).

[2] Broadbridge and Edser, U.S. 1,505,944 (1924); Bailey, U.S. 1,770,476 (1930); Mertens, Brit. 328,606 (1928); U.S. 1,853,871 (1932) and 1,937,291 (1933).

[3] *Ind. Eng. Chem.*, **17**, 837 (1925); Brit. 197,033 (1922).

[4] U.S. 1,325,873 (1919).

[5] *Ind. Eng. Chem.*, **21**, 210 (1929).

[6] *Ind. Chemist*, **8**, 175 (1932). By courtesy of the Editor this account is reproduced. See also Smith, *J. Soc. Dyers Colourists*, **49**, 241 (1933).

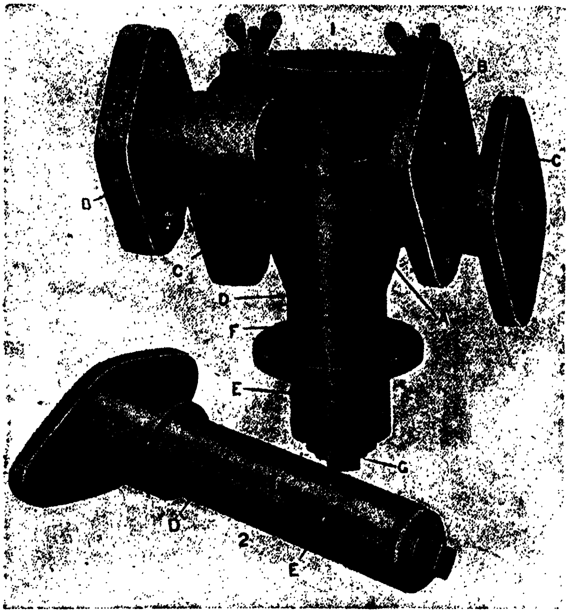

FIG. 87. The Barber Jet.

The thick foamy grease is washed with water to remove occluded soaps and dirt; finally, it is boiled with water. The grease is now autoclaved at between 120° and 130° C. The feed tube containing alternate perforated and non-perforated plates is situated axially in the autoclave. The grease and liquor are fed in at the bottom, and are forced to take a zigzag path through these plates, thus assisting further the separation of grease from water. The mixture overflows the top plate down an annulus and up again into the main body of the autoclave, where the floating grease and the water are separately removed. A perforated steam pipe is supplied in the base of the autoclave to remove sludge.

BUTTER

The preparation of butter affords an excellent study of the breaking of an apparently stable emulsion by merely agitating, due to a new distribution of emulsifying agents. The act of churning cream to form butter is most intimately related to the formation of foam (see p. 17).

Cream is agitated in a churn, thickening thereby until it has a pronounced rigidity. The fat aggregates grow in size and enmesh the milk serum. At the same time the air incorporated by the agitation produces a foam which assists the resistance of the churn contents to agitation. A point is suddenly reached in churning when the fat agglomerates have reached dimensions when further entrainment of liquid ceases and the butter "comes," whey recedes off the butter clumps, and many butter granules become visible to the naked eye. Churning occupies 40 to 60 minutes, but the butter "breaks" or "comes" with amazing suddenness. The butter granules are afterwards worked or pressed to a homogeneous fatty mass.

The physical conditions of churning, especially the temperature, exert a profound influence on the butter, particularly with regard to its moisture content. The main factors to be considered in this connection are the fat content, the acidity, and the viscosity of the cream, and the agitation employed. Jørgensen [1] points out that other factors influencing the yield are the size of the fat globules and the extent of their clumping together in cream. Cream with large fat globules churns the easiest, an observation confirmed by Van Slyke,[2] whose study showed that milk from breeds giving the larger globules churned the more readily, and that churning was more prolonged as the lactation period increased.

A cream containing 30–45 per cent. of fat churned at a temperature ranging from 13°–18° C. should give good results. As cream ripens, lactic acid is produced, the viscosity of the cream diminishes and churning becomes easier. The casein is coagulated and precipitated if the acidity is too pronounced, and casein clots may be found in the butter mass. Hittcher [3] found that the initial churning temperature of the cream and its fat content have hardly any influence on the size of the agglomerates of butter formed. He made the interesting observation that freezing the cream prior to churning at usual temperatures greatly accelerated churning. Probably this is due to some change in the physical characteristics of the protein envelope.

Guthrie and Sharp [4] investigated the relation between the *p*H value of the cream and the time required for churning. They found that hydration or dispersion of the casein resulted in a longer time for churning, whilst dehydration or precipitation was associated with a reduction in the churning time.

The work of King [5] has shown that butter is a solid system with a fatty continuous phase in which are dispersed fat globules, water globules and air bubbles, all enveloped by hydrated protein. In all probability the fatty continuous medium is the more liquid fraction of butterfat, pressed out from the fat globules during churning and subsequent working. The general emulsion type is that of water-in-oil.

The fundamental initial problem [6] presented by butter is concerned with the conversion of cream, an O/W emulsion, to butter, a W/O system. Earlier views were that the mechanical action of churning split open the layer of emulsifying agent, liberating the globules of the fatty phase.[1]

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[1] *Molkerei Ztg.*, **40**, 1772 (1926).

[2] N.Y. (Geneva) Agr. Expt. Sta., 10*th Intern. Rept.* (1891), p. 385.

[3] *Landw. Jahrb. Schweiz.*, **51**, 489 (1918). See Sharp, *J. Dairy Sci.*, **23**, 775 (1940).

[4] *J. Dairy Sci.*, **14**, 1 (1931).

[5] *Kolloid Z.*, **52**, 319 (1930); *Lait*, **12**, 675 (1932); *Milchwirtschaft. Forsch.*, **15**, 231 (1933). Similarly, see van Dam and Holwerda, *Verslag. landb. Onderzoek.*, **40** C., 175—213 (1934), and the recent work of Storgårds, *Dairy Sci. Abstracts*, **2** (i), 80 (1940).

[6] See Trolle, *Svenska Mejeritidningen*, **23**, 281 (1931), who deals with mechanical coagulation; Mohr, *Z. Unters. Lebensm.*, **66**, 37 (1933), on the technique of butter-making; Schwarz, *Z. angew. Chem.*, **47**, 481 (1934), on the physico-chemical reactions in butter-making; Manhart, *J. Dairy Sci.*, **11**, 52 (1928), on the variability in composition of butter from the same churning in relation to working. Coulter and Combs, *ibid.*, **17**, 551 (1934)

From the modern schools two outstanding theories have been proposed: (1) the Phase-Inversion Theory; (2) the Foam Theory.

THE PHASE-INVERSION THEORY

The Fischer-Hooker Theory of emulsions (see p. 194) has been applied to milk and butter.[2] Milk is considered as an emulsion of butterfat in hydrated protein. Full cream milk shows little tendency to form butter, nor even does cream. According to Fischer and Hooker, the tendency of cream to form butter is assisted by the dehydration of the protein with which the water is so combined, *e.g.*, by souring the cream. They write: " Since the hydrated colloids tend to collect in the surface layers between the fat particles and the aqueous phase of the cream, efforts are made to break these layers, and so to hasten coalescence of the fat droplets, by churning. *The combined efforts therefore bring about a progressive increase in the concentration of the oil with a decrease in the concentration of the hydrated colloid until the instability of the oil-in-hydrated colloid emulsion becomes so great as to ' break ' and yield the hydrated colloid-in-fat emulsion which we call butter.*"

Palmer [3] supports this theory, studying the inversion of emulsion type by staining the fat globules in cream with oil-soluble dyes before churning. He [4] also demonstrated by electrical conductivity measurements that the resistance of cream at constant temperature during churning increases to a maximum, remains stationary for about 30 minutes, and then drops rapidly to the original value. The point of maximum resistance is identified with the completion of the gradual inversion of the phases. The " breaking " of the butter and the release of the buttermilk at once restore the electrical conductivity.

The present writer would point out that true inversion of emulsions is not indicated. There is a release of the fat globules from their protein environment, and this release would result in a complete fat separation did the fluidity of the fatty phase permit. (Thus, North [5] agitates cream until the fat globules agglomerate and then treats with hot water so as to separate the butterfat as an oily layer.) One cannot consider churned cream with its butter granules as an emulsion at all; it is, in fact, a suspension of loose fatty granules within which the aqueous medium is also enmeshed. By purely mechanical working these granules are pressed together so that the homogeneous butter mass contains aqueous globules because of incomplete expression of buttermilk. The resemblance of

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investigate the relation of the composition of butterfat to the churnability of cream, whilst Wiley, *J. Council Sci. Ind. Research*, **12**, 391 (1939), deals with the butter losses in churning.

[1] Churning is not the only mechanical means of making butter. Perks subjects a stream of cream to repeated impact through vibratory motion imparted to the stream in a direction perpendicular to its surface; Brit. 322,416 (1929); U.S. 1,791,000 (1930).

[2] " Fats and Fatty Degeneration " (New York, 1917), p. 93.

[3] Missouri Agr. Expt. Sta., *Bull.*, **163**, 40 (1919).

[4] *Colloid Symposium Monograph*, **1**, 411 (1923).

[5] Brit. 206,918 (1922); U.S. 1,416,053 (1922).

butter to a water-in-oil emulsion is thus accidental. What really demands explanation is why milk or cream emulsions lose stability or *break* (not invert) upon being agitated, and the Foam Theory seeks to provide such explanation.

THE FOAM THEORY

As already stated, the violent churning of cream causes the incorporation of air and the formation of a foam. Then quite suddenly the foam collapses and almost simultaneously the butter nuclei grow to macroscopic size. Siedel showed that in churned cream prior to the foam collapsing, nearly all the fat had accumulated in the foam and the liquid menstrum had become very poor in fat. Also, he proved that cream from churned milk which no longer frothed would not yield butter. On the basis of these observations and a study of skim milk froth, Rahn [1] proposed the following theory of butter formation.

In the fat-rich foam of churned cream there is a close packing of the fat globules in the froth lamellæ, finally leading to fat clumps. The protein in the froth lamellæ gradually assumes a solid character (irreversible), and continued churning destroys the structure, whereupon the foam collapses. Further working brings about the gradual union of the fat globules and simultaneously with the collapse of the foam the fatty agglomerates are large enough to become visible ; the two phenomena have a common origin.

Practical experience supports this theory. Butter can be made even at temperatures where the fat is quite liquid, and Rahn's theory shows no necessity for the fat to be solid. Foam formation and " precipitation " of the foam-colloid occur at higher temperatures.

The highest limit for butter formation (34° C.) is fixed by the mechanical breaking down of the fat globules and the newly-formed butter nuclei. This rapidly increases with rising temperature so that at 50° C. after churning new milk for 1 hour, 83–87 per cent. of the fat, and after 2 hours' churning 100 per cent. of the fat, is completely homogenised and will not separate from the skim milk when centrifuged.[2]

Rahn [3] has shown that the inability to churn cream at low temperatures is due to the non-cohesion of the solid fat globules, although at even 2° C. there is distinct evidence of a clumping tendency. He mentions, too, that a full churn with no air space will not yield butter even after two hours' agitation. Rahn's theory receives additional support from experiments by Pedersen,[4] who washed cream with water prior to centifruging and then subjected the cream to bacterial action to effect changes in the protein content. Such cream would not churn into butter. Pedersen also made an emulsion of butterfat in skim milk, dispersed to a degree comparable with fresh milk. Churning was very difficult to accomplish, and butter formation was incomplete. The resulting butter resembled margarine.

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[1] *Kolloid-Z.*, **30**, 341 (1922) ; " Physik der Milchwirtschaft " (Berlin, 1928), p. 81 *seq.*; " Die Butterbereitung," Sonderdruck aus " Handbuch der Milchwirtschaft," by Grimmer and Weigmann (Wien, 1931), pp. 41—139. This report contains an extensive bibliography.

[2] Siegfeld, *Molkerei-Ztg.*, **22**, 287 (1908).

[3] *Kolloid-Z.*, **30**, 341 (1922).

[4] *Molkerei-Ztg.* (1918), 176.

Finally, Rahn showed that a thin layer of butter left under the microscope for a few days gives a clear edge due to water evaporation, and in this clear rim can be seen the delicate outline of the envelopes of individual fat globules, which according to the treatment of the butter are still more or less spherical. The further work of King[1] gives strong support to these findings.

Investigations in Palmer's laboratory have thrown doubt on Rahn's theory. It was firstly[2] shown that fresh buttermilk contains some material or materials capable of promoting O/W emulsions. Some at least of this material must have come from the surface of the fat globules in the cream whilst churning. Later,[3] it was proved that the adsorbed layer on the globules is a mixture of phospholipides and protein. Such surface-active material is recoverable from the buttermilk even when the cream has previously been washed free of all water- "soluble" material prior to churning. Palmer mentions confirmation of experiments by Mohr and Brockmann,[4] who found that whilst foaming was essential in order to obtain butter from sweet fresh cream, the churning of sweet aged and of sour cream could be carried out in a full churn, *i.e.*, without frothing. Again, cream obtained from sweet buttermilk could be churned.

Palmer believes that not only does the foam theory require modification, " but that an inversion of phases does take place during some stage of the butter-making process." Coagulation of the protein membrane is not accepted—" the largest part of the colloidal material exhibited no evidence of coagulation."

The present writer is of the opinion that the loss of stability of the original cream emulsion is definitely due to some denaturation change in the protecting material, and such denaturation precedes the visible piling stage or coagulation. Frothing can effect such denaturation and so can acidity or ageing; thus, frothing need not be essential with old or sour cream. Controlled agitation of an emulsion with an air space in the container is a routine test for emulsion stability in the writer's laboratory. The emulsion is held on a wheel (Fig. 88), rotating about 15 times per minute. Breaking of an emulsion is definitely related to the incidence of an air space, and even so, is only observed when the emulsifying agent is of such a nature as to undergo change at an air/water interface. Salad dressings stabilised with egg proteins respond easily to this test, whilst gum-stabilised emulsions fail to break under the same conditions.

Investigations in the present writer's laboratory have clearly settled the issue in favour of Rahn's theory. On thermodynamical grounds, if there are two agents present in a system, each of them capable of foaming, the one that is the more surface-active or foam-forming will preferentially accumulate at the air/liquid interface. Hence, if to cream there be added a very surface-active material, churning would proceed practically indefinitely without butter formation, since the new agent will prevent the milk colloids gaining access to the air/liquid interface. There will be foam, but it will not be milk foam. Experimentally, this idea has been markedly successful.[1]

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[1] *Milchwirtschaft. Forsch.*, **8**, 93, 423 (1929).
[2] *J. Dairy Sci.*, **15**, 371 (1932).
[3] *Ibid.*, **16**, 41 (1933); **17**, 29 (1934).
[4] *Milchwirtschaft. Forsch.*, **10**, 173 (1930).

Following Palmer, the electrical resistance of the cream was measured during churning. Normally, churning occupied about 60 minutes with fresh cream of 50 per cent. fat content held at 16° C. Loading the cream with sucrose to a concentration of 50 per cent. in the water phase, so as to increase the density difference between the phases, caused dramatic churning in 15 minutes.

The addition of saponin to the cream greatly prolonged the time for churning. As little as 1 in 500,000 of saponin increased the time of churning of the fresh cream to 175 minutes, whilst with 1 in 10,000 of saponin churning was not evident after 240 minutes. Even with the added sucrose the presence of 1 in 1,000 of saponin delayed churning for at least 300 minutes (the duration of the test).

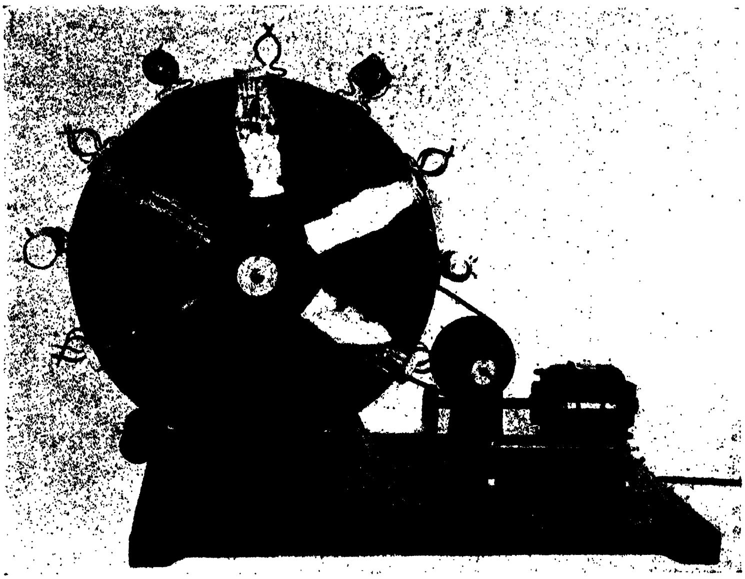

FIG. 88. Rotating wheel for testing emulsion stability (Clayton).

More striking was the effect of egg albumin, again surface-active but itself undergoing denaturation when foaming. It was argued that if egg albumen was added to cream, its influence to inhibit churning would persist only until surface denaturation had removed it from solution. The course of the electrical resistance in a test with 0·5 per cent. of egg albumen in fresh cream furnished excellent confirmation of this theory (Fig. 89). In confirmation also was the fact that adding non-surface-active colloids to cream, *e.g.*, 1 per cent. of gum arabic, failed to affect the churning process at all.

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[1] Clayton and Morse, *Nature*, **139**, 717 (1937); *Kolloid-Z.*, **80**, 31 (1937); *Food*, **6**, 475 (1937).

These results bear directly on the delayed churning of cream often encountered in cream separated from the milk of cows in advanced lactation. Thus Krukovsky and Sharp[1] have discussed the effect of lipolysis on the churnability of such cream. Lipolytic action leads to cream with a new frothing capacity; the fatty acids and soaps displace the normal foam constituents at the plasma/air interface, and churning is delayed.

Although the foam theory must be regarded as established without doubt, it must be conceded that there yet remains an explanation of the actual changes taking place in the foam constituents. Sandelin[2] investigated the influence of soap and lecithin on the stability of artificial cream during churning. Thus 0·025 per cent. of lecithin would emulsify 4 per cent. of butterfat. Neutral or faintly alkaline emulsions foamed strongly and when the foam broke the draining liquor was less acid than the foam itself. Butter separated from the "cream" as the lecithin layer around the fat globules was removed or became thinner. Collection of the unprotected fat globules into clumps then followed.

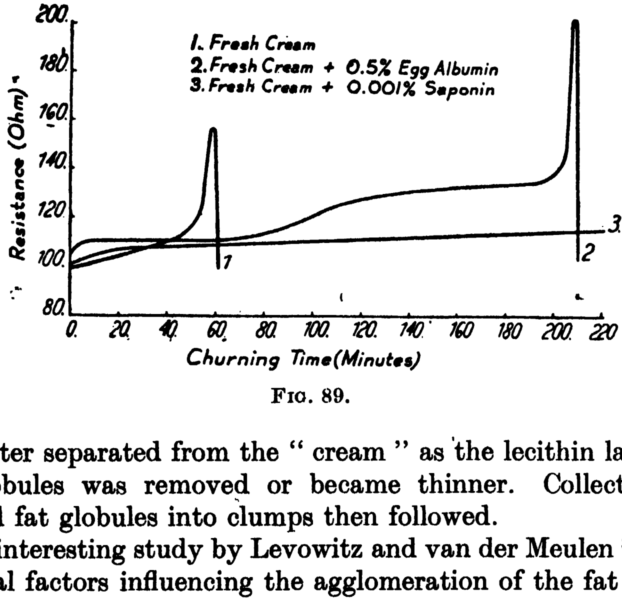

FIG. 89.

A most interesting study by Levowitz and van der Meulen[3] concerned the principal factors influencing the agglomeration of the fat globules in a foam and their possible subsequent coalescence: (1) viscosity of the interglobular liquid as affecting drainage of liquid from the foam structure; (2) thickness and nature of the adsorbed film around the globules; (3) electric charge on the globules. Churning time was little influenced by factors (1) and (3).

The authors conclude that instead of assuming an irreversible coagulation of a hypothetical foam substance, "as a result of the mechanical action of the churn the stabilising films of some of the fat globules are broken, liberating the oil from the least stable globules, but leaving the more stable globules essentially unchanged. The free oil produced by the rupture of the least stable globules forms a cementing material for the stable globules in its immediate vicinity."

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[1] *J. Dairy Sci.*, **19**, 279 (1936). See also Palmer, *ibid.*, **5**, 201 (1922); Tarassuk and Richardson, *ibid.*, **24**, 667 (1941), and Sharp, *ibid.*, **23**, 776 (1940).

[2] *Chem. Zentr.*, **1939, II**, 2181.

[3] *J. Dairy Sci.*, **20**, 657 (1937).

If only a proportion of the globules are thus involved in churning, any condition in which a part of the globules are caused to set free their fat in the presence of stabilised globules should produce butter. Levowitz and van der Meulen actually proved this argument by taking 40 per cent. cream, diluting it with 10 volumes of water, warming to about 54° C. and slowly centrifuging (the cream outlet of the separator being warmed to maintain liquidity on the butterfat). Butter issued from the separator, the consistency being a function of the dilution and temperature of the cream. That it was butter was demonstrated by non-redispersion when stirred in water and by identification by skilled butter workers.

CENTRIFUGAL SEPARATION OF EMULSIONS

Both emulsions of the oil-in-water and the water-in-oil types can be separated into oil and water by suitable centrifugal treatment, which depends on the difference in specific gravities of the two phases.[1]

On the whole, industrial emulsions are always capable of being separated by centrifugal machines, since the emulsified particles are sufficiently large for such treatment. Frequently the viscosity of the dispersion medium is the main factor for consideration and heat may be necessary before the more stable emulsions can be centrifuged. Sometimes a partial chemical or electrical coalescence must precede centrifugal separation.

Centrifugal separators date from about 1850, but the first continuous centrifugal separator was invented by Gustaf de Laval in 1878, and was applied to the separation of cream from milk. Since the modern de Laval machine is employed in numerous industries with recognised efficiency, this type will be discussed in some detail as being typical of ordinary centrifugal practice. As a special case, its application to cream separation may be taken. It is to be emphasised that breaking of the emulsion (milk) is not effected, but rather a concentration of the emulsion.

CENTRIFUGAL SEPARATION OF CREAM

Separation of an emulsion of fat in aqueous medium depends on the difference in specific gravity of the two phases. Centrifugal separation [2] is an enhanced gravity settling, the gravitational force being enormously magnified. The fat globules move through the aqueous phase with a velocity influenced by such factors as (1) centrifugal force exerted; (2) viscosity of the aqueous medium; (3) difference in the density of the phases; (4) relation between the mass and the surface area of the globules; (5) temperature.

[1] Centrifugal separation is well described by Olive, *Food Inds.*, **9**, 229 (1937). Piddlesden deals with the concentration of latex by centrifugal machines: *J. Rubber Research Inst. Malaya*, **10**, *Commun.* 250, 78—107 (1940). The patents granted are numerous, but recent trends will be seen in: Lindgren, U.S. 2,005,094 (1935); Aktiebolaget Separator, Brit. 425,656 (1935); Bergedorfer Eisenwerk A.-G., Brit. 425,753 (1935); Maschinefabrik Chem. A.-G. and Egg, Brit. 451,492 (1936); Schelbeck, U.S. 2,087,630 (1937); Lindgren, U.S. 2,195,730 (1940); U.S. 2,174,272 (1939).

[2] Ayres, *Ind. Eng. Chem.*, **13**, 1011 (1921); Mork, *Meldinger Norges Landbruks*, **7**, 1—60 (1927); Killeffer, *Ind. Eng. Chem.*, **19**, 287 (1927).

From Stokes' equation it is obvious that although the specific gravity difference is important, such importance rapidly diminishes when the diameter of the globule is sufficiently reduced, since the velocity is proportional to the square of the radius.

The separation of cream may be effected in many types of centrifugal separators, and the following discussion will be based on the use of the modern de Laval type.[1]

The essential part of the machine is a bowl, capable of being revolved at high speed, containing a series of round, sloping, conical steel discs, superimposed and spaced slightly apart by thin calks or ribs fastened to them. Milk is fed into the centre of the bowl by a distributing device contained in the central shaft, and passes through tangential slots in the wall of the shaft into enclosed gutters. It now flows from the lower ends of these gutters (which extend beyond the cream wall), and is delivered into the neutral zone or separating disc space of the bowl, passing upward into the various discs through a series of openings in the discs located above and in line with the distributing device outlets. The important result is thus obtained of delivering the incoming milk into the separating discs without interference of the cream wall or mixing of the incoming milk with the already separated cream. The separation then takes place in the discs, the cream particles moving inward toward the centre and forming the cream wall round the central shaft and distributing device and mounting upward to the point of discharge through the cream outlet. The skim milk moves outward beyond the discs and is carried upward along the wall of the bowl to the points of discharge through the skim milk outlets (see Fig. 90).

It can be shown[2] that under the influence of centrifugal force, the time required for a globule of radius r to travel through a given space is proportional to the square root of the cube of the radius, *i.e.*, $r^{3/2}$. As the number of gallons of milk handled per hour by the machine is inversely proportional to the time, it follows that for any given radius of globule there is a critical value where its velocity against the stream of milk will be equal to the velocity of the stream itself, so that globules of smaller radius pass out with the stream of separated milk. The fat content of the separated milk is proportional to the cube root of the square of the number of gallons per hour.

Centrifugal machines for cream separation are usually run at 6,000 revolutions per minute.[3] The intensity of the centrifugal force exerted is directly proportional to the mass of the contents of the bowl, to the diameter of the bowl, and to the square of the speed of revolution.[4] The ratio of cream to separated milk will depend on the relative distances of their respective outlets from the centre of the bowl under normal running conditions.

An important figure in cream separation is the capacity of the separator, *i.e.*, the quantity of milk which can be separated per hour. Obviously this depends on the centrifugal force and on the rate of inflow of the milk. Any increase over the optimum capacity will lower the efficiency of the separator, since the milk will necessarily be subjected to centrifugal action for a shorter period ; this means a loss of butterfat carried away in the separated milk. The rate of inflow of the milk requires careful control ; reduction of the rate below the normal value does not lead to increased efficiency of separation, merely lengthening the time required.

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[1] See also Happgood, U.S. 2,145,544 (1939); Sharp, *J. Dairy Sci.*, **23**, 774 (1940).

[2] Richmond, "Dairy Chemistry" (London, 1914), 255—9; Sharp and Troy, *J. Dairy Sci.*, **11**, 259 (1928).

[3] *Vide* Hunziker, "The Butter Industry" (1927), 77—97.

[4] *Milchwirtschaft. Forsch.*, **2**, 382 (1925).

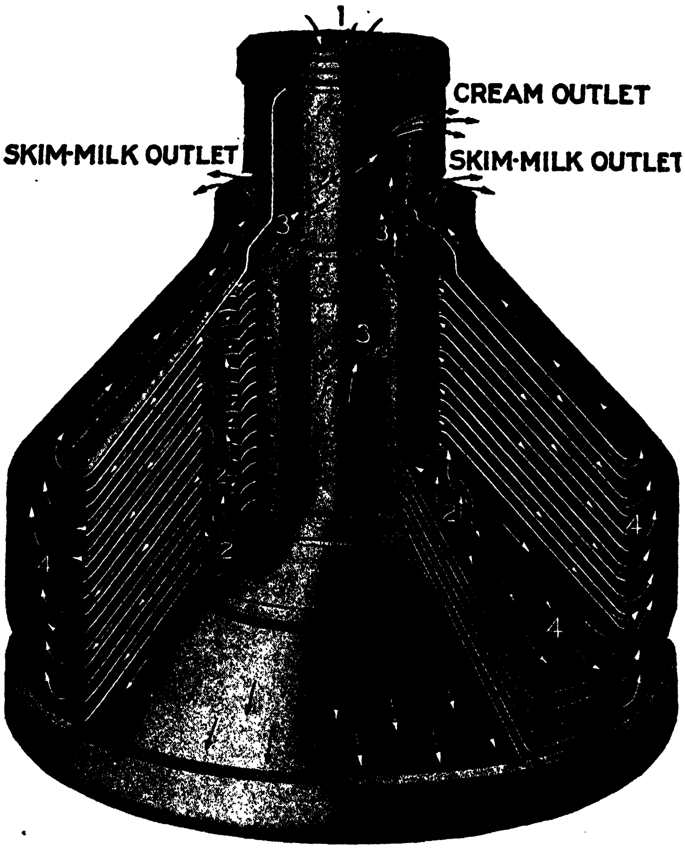

FIG. 90. Cross-section of de Laval cream separator.

Cream is usually separated at 29°—35° C. At lower temperatures the viscosity of the milk increases and the fat globules are influenced by the greater resistance offered to the centrifugal separation. Though the cream is richer, due to the slower passage of the milk through the machine, the loss is greater, since the separated milk contains more than the usual amount of fat.

The quality of the milk is important. The richer it is in butterfat, the richer is the cream and the greater the loss in the skim milk. As an approximate guide, the percentage of butterfat in the cream is proportional to the fat content of the whole milk.

Sharp[1] has made an interesting study of the physical constants of milk as influencing the centrifugal separation of cream at different temperatures. He shows that the rate of movement of a fat globule through the milk plasma due to centrifugal force at any instant is given by the equation :—

$$V = \frac{2r^2(d_p - d_f)4\pi^2 n^2 R}{9\eta 3600}$$

or

$$V = \frac{0{\cdot}00244(d_p - d_f)r^2 n^2 R}{\eta},$$

where r = radius of the globule.
η = viscosity of the milk plasma.
d_p = density of the milk plasma.
d_f = density of the fat.
n = number of revolutions of separator bowl per minute.
R = distance of the fat globule from the axis of rotation.

If K be a constant covering all the factors in the equations, which are independent of the dimensions and speed of the separator and the size of the globules,

$$K = \frac{0{\cdot}00244\ (d_p - d_f)}{\eta}.$$

Under the constant operating conditions, the effective force tending to the separation of the fat globules depends on the magnitude of K, and would thus be more effective the greater the difference in density of the phases and the lower the viscosity. Both factors are influenced by temperature, and the following table by Sharp illustrates this.

TABLE 53

DENSITY OF PLASMA AND FAT, AND THE VISCOSITY OF THE PLASMA AS AFFECTING THE VELOCITY OF MOVEMENT OF THE FAT GLOBULES UNDER CENTRIFUGAL FORCE

Temp.	d_p	d_f	$d_p - d_f$	η	K	K^1	Percentage Increase in K^1 per 5° C. Rise in Temp.
0° C.				Poise.			Per cent.
5	1·0365	0·9612	0·0753	0·0296	0·0062	0·0062	—
10	1·0359	0·9528	0·0831	0·0247	0·0082	0·0083	33·0
15	1·0348	0·9421	0·0927	0·0210	0·0108	0·0110	33·0
20	1·0338	0·9304	0·1034	0·0179	0·0141	0·0144	30·9
25	1·0322	0·9208	0·1114	0·0154	0·0176	0·0181	25·9
30	1·0306	0·9119	0·1187	0·0133	0·0218	0·0226	24·9
35	1·0288	0·9082	0·1206	0·0117	0·0252	0·0262	15·9
40	1·0266	0·9050	0·1216	0·0104	0·0285	0·0297	13·4
45	1·0245	0·9012	0·1233	0·0093	0·0323	0·0337	11·3
50	1·0223	0·8982	0·1241	0·0085	0·0356	0·0372	10·4
55	1·0198	0·8945	0·1253	0·0077	0·0396	0·0415	11·4
60	1·0171	0·8913	0·1258	0·0071	0·0432	0·0454	9·1
65	1·0145	0·8881	0·1264	0·0066	0·0467	0·0492	8·4
70	1·0117	0·8848	0·1269	0·0062	0·0499	0·0527	7·1
75	1·0086	0·8813	0·1273	0·0059	0·0526	0·0558	5·9
80	1·0054	0·8778	0·1276	0·0057	0·0546	0·0580	3·9

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[1] *J. Dairy Sci.*, **11**, 259 (1928).

The most marked difference in phase densities occurs between 5° C. and 35° C., the increase being rapid, whilst the viscosity decreases somewhat rapidly up to about 40° C. Thus K increases rather rapidly with rise in temperature up to the range 35° C. to 40° C.; it is not so pronounced thereafter. "Still another factor which tends to make the efficiency of separation increase more rapidly with temperature up to 35°—40° C. is the actual expansion of the fat globules. If the size of the fat globules is measured at 5° C., their volume will be 6·2 per cent. greater at 40° C., while they will increase in volume only about 3 per cent. in going from 40°—80° C. It was assumed that the fat globules were measured at 5° C. and the effect of the increase in size of the fat globules with the increase in temperature as influencing K is given as K^1."

Crude oil-field emulsions provide another interesting industrial application of centrifugal separation. Some American centres still prefer this method of separation to electrical dehydration. Ayres[1] has pointed out that centrifugal separation has two related advantages over simple gravity settling. Firstly, "if the centrifugal force is from 15 to 18 thousand times as great as the force of gravity, the gravity separation will take 15 to 18 thousand times as long as the centrifugal. The emulsions in Kansas, Oklahoma and some parts of Texas require the exertion of a force of this magnitude to effect subsidence in 1 in. layers during a period of from 6 to 18 seconds. The corresponding figures for gravity are from 24 hours to 3 days." The second advantage is that, owing to the enormous reduction in the time required for subsidence, an emulsion may be heated for this brief period at a permissible cost, so enhancing coalescence at the higher temperature as to yield all the water as a homogeneous phase. Sometimes, instead of heating the original emulsion, it is first centrifuged at ordinary temperatures, and then the effluent (concentrated) emulsion is heated to cause coalescence prior to further centrifugal separation.

THE SHARPLES SUPER-CENTRIFUGE

The super-centrifuge has also been introduced into oil-field practice.[2] The revolving bowl is a steel cylinder, 4½ in. in diameter, 30 in. long and weighing 35 lb. It is contained within a conical cast-iron casing, and is so driven that a speed of 17,000 revolutions per minute is attained. The bowl is suspended from a ball-bearing by means of a flexible spindle, and at the foot is guided in a bushing designed simply to limit any lateral movement that may develop. Inside the bowl, attached to its upper end, is a three-winged vane, the purpose of which is to prevent the liquid being dealt with from slipping relatively to the bowl, and so losing some of the centrifugal effect. The liquid to be treated is admitted by a pipe to a jet at the centre of the guide bush at the foot of the bowl. A band brake is provided for bringing the bowl to rest after a run.

Fig. 91 illustrates the action of the apparatus. The jet of emulsion, on entering the bowl, strikes a horizontal circular baffle plate, which spreads it out sideways. Under the influence of centrifugal force, the liquid piles up round the cylindrical surface of the bowl, leaving an air space in the interior. If the liquid consists of a lighter and a heavier component, such as a mixture of oil and water, it will stratify, the lighter constituent keeping to the interior and the heavier going outwards. A ring at the top of the bowl—the ring from which the three-winged vane is suspended—permits the two strata to be separated, the lighter liquid going through the centre of the ring and the heavier passing round its periphery. The two streams find their exits through separate passages in the head and flow into collecting chambers provided with spouts. A third stratum, containing the solid impurities, forms, as indicated, at the foot of the bowl, and there collects until removed at the end of the run. The heavy liquid, just before it leaves the top of the bowl, has to pass a dam ring, the clearance here provided being variable to suit differences in the relative specific gravities of the two liquid constituents. If zero clearance

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[1] *Ind. Eng. Chem.*, **13**, 1011 (1921). Cf. *Chem. Met. Eng.*, **22**, 1057 (1920) and Meston, *Oil and Gas J.*, **22** (xx), 56 (1923).

[2] Born, *Ind. Eng. Chem.*, **13**, 1013 (1921). Cf. Keable, *J. Oil Colour Chem. Assocn.*, **5**, 2 (1922).

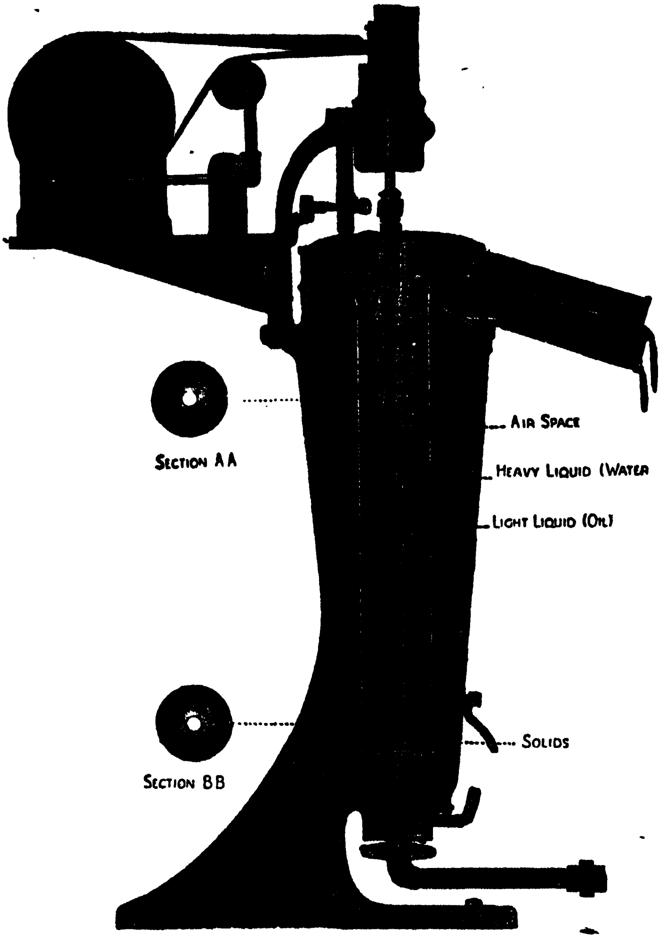

Fig. 91. Illustrating the action of the Sharples super-centrifugal oil purifier.

is provided at this point, the apparatus acts as a clarifier for liquids comprising a single constituent and solid impurities.

Several constructional features of the apparatus are of interest. The motor, of about 2½ h.p. and running at 3,450 revolutions, drives the pulley at the top of the flexible spindle through a form of woven cotton belt, which is kept taut by a jockey pulley and weight. In some applications the motor is dispensed with, and the bowl driven by a small steam turbine, mounted with its wheel horizontal at the top end of the flexible spindle. The collecting covers are held stationary on top of the conical casing by means of a hinged member with a felt pad at its foot. The hand brake is thrown into action by the movement of a lever on the outside of the casing, but the pressure applied by it is controlled, not by this lever, but by a spring which the lever releases. The guide bush at the foot of the bowl is lubricated by the fluid being operated upon, if that fluid happens to have lubricating properties. If such is not the case, the design is modified to exclude the fluid from the bush and to admit lubricant through a separate channel.

Besides possessing the advantage of greater speed and enhanced centrifugal force, the super-centrifuge permits a longer application of centrifugal force to the emulsion particles, owing to the elongated bowl. The emulsions are gravity-fed to the separator under a head of about 30 ft., being previously heated to 110°—180° F. (43°—82° C.). In starting up, the bowl is revolved slowly and brine admitted until full speed is attained, when emulsion is run in continuously. About 100 to 200 barrels of dehydrated oil can be obtained from one machine in twenty-four hours. Even " bottom settlings " containing 70—80 per cent. of water can be cleared to oil containing as little as 0·5 per cent. water.

James [1] has given a comprehensive account of the use of the super-centrifuge in industry. Other literature refers to the centrifugal separation of oil from condenser water,[2] the separation of water from oils for varnish manufacture,[3] the preparation of a plastic cream containing over 65 per cent. of butterfat,[4] and a study of the effect of speed of rotation, length of testing bottles and diameter of rotor on the determination of fat in dairy products.[5]

[1] Alexander's " Colloid Chemistry," Vol. 3 (New York, 1931), p. 206.

[2] Fischer, *Warme u. Kalte Tech.*, **25**, 69 (1923).

[3] Ebel, *Seifensieder Ztg.*, **51**, 307, 327 (1924).

[4] Wendt, U.S. 1,791,068—9 (1931); Mack and Foskett, *Food Ind.*, **6**, 156 (1934).

[5] Roeder, *Milchwirtschaft. Forsch.*, **13**, 5 (1932).

CHAPTER XIII

PHYSICAL MEASUREMENTS IN EMULSIONS

THE study of emulsions in the laboratory frequently involves the determination of surface and interfacial tensions, the nature of the internal or external phase, the concentration of the emulsion, and the degree of dispersion.

DETERMINATION OF SURFACE TENSION AND INTERFACIAL TENSION

For colloid phenomena in general and emulsion studies in particular, the determination of surface tension and interfacial tension is of fundamental importance. Numerous methods have been devised,[1] several of which will now be selected because of their accuracy or their simplicity for technical routine work.

It should be understood that when dealing with colloid systems there is an interface-ageing effect, *i.e.*, the establishing of an interface-adsorption equilibrium. In consequence, the methods of determining surface or interfacial tension give results depending on their disturbance or otherwise of the surface or interface. Rapid measurement of a disturbed surface (*e.g.*, by the method of vibrating jets or ripples) will give higher values than with undisturbed surfaces (capillary rise, study of drop-curvature or dimensions). The former methods give the so-called dynamic values, the latter the static values.

THE CAPILLARY RISE METHOD

Very accurate results for the static surface tensions of liquids are possible with this method,[2] provided extreme care is exercised in control of temperature, tube calibration, cleanliness of apparatus, etc. The principle involved is that when a glass capillary tube dips into water, the water rises inside the tube and the following relation holds :

$$\sigma = \tfrac{1}{2}rhg\,(d - d').$$

where σ = surface tension.

r = radius of tube.

h = height of liquid in the tube measured from the bottom of its meniscus and the surface of the main bulk of liquid.

d = density of the liquid.

d' = density of the vapour phase.

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[1] Critical summaries are given by Ferguson, *Manc. Memoirs*, **65** (1921), No. 4; *Sci. Progress*, **9**, 428 (1914—15); *Trans. Faraday Soc.*, **17**, 370 (1922); *J. Sci. Instruments*, **10**, 34 (1933); Lenard *et al*, *Ann. d. Physik.*, 4th Series, **74**, 381 (1924); Hiedemann, *Z. physik. chem. Unterricht*, **44**, 1 (1931); Dorsey, *Bull. Natl. Research Council*, No. **69** (1929).

[2] Ramsay and Shields, *Z. physik. Chem.*, **12**, 433 (1893). For mathematical discussion see Porter, *Phil. Mag.*, **7**, 624 (1929); **17**, 511 (1934); **21**, 703 (1936); **26**, 519 (1938). A critical study of the wetting action of liquids in capillaries is given by Loman, *Chem. Weekblad.*, **36**, 337 (1939); see also Nellensteyn, *ibid.*, **36**, 146 (1939). Bosanquet, *Phil. Mag.*, **5**, 296 (1928), also treats of the equation for the form of a liquid surface at rest in a circular tube under the influence of capillary forces and gives tables of appropriate quantities

Complete experimental details of most careful experiments are recorded by Volkmann,[1] Richards and Coombs,[2] Richards and Carver,[3] Harkins and Brown,[4] and Sugden.[5]

Morino [6] employed this method throughout an extensive study of the surface tensions of liquids and liquid mixtures, modifying the apparatus so that density measurements could be determined in the same vessel in which the height h had been observed.

It is essential to hold the capillary tube vertical in order to avoid distortion of the meniscus, which must be as nearly circular as possible. The angle of contact must be known and, preferably, should be zero. The calibration and the cleaning of the capillary tube present considerable difficulties.

A method demanding so much from its users is not suitable for general work, and has led Ferguson and Dowson [7] to propose the simple modification, viz., instead of measuring the capillary rise, one can force the liquid down to the lower end of a tube immersed vertically in the liquid, and measure, on a convenient manometer, the pressure required to do this. Thus calibration troubles are avoided, quite a short piece of capillary tubing may be used, and thermostatic control is facilitated. The equation given by Ferguson is :

$$\sigma = g\frac{r}{2}(d_1h_1 - d_2h_2) + gd_2\frac{r^2}{6}.$$

where σ = surface tension.
r = internal radius of tube at the tip.
h_1 = manometric pressure in centimetres.
d_1 = density of manometric liquid (paraffin) in grams/cubic centimetres.
h_2 = depth of immersion of the tip in the liquid examined.
d_2 = density of the liquid examined, in grams/cubic centimetres.

For pure benzene, the value σ = 29·66 dynes/cm. was obtained, in excellent agreement with the most careful experiments of Harkins and Brown and Richards and Coombs. The method has been successfully used by Edwards,[8] Ferguson and Hakes,[9] and Ali.[10]

Speakman [11] modified the method to advantage by using *two* capillary tubes of different bores and noting the *difference* between the pressures

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necessary to solve it. Related are important papers by Peek and McLean, *Ind. Eng. Chem., Anal. Edn.*, **6**, 85 (1934), and Schultze, *Kolloid-Z.*, **55**, 9 (1931). A modification of the capillary rise method of measuring the surface tension of solutions relative to that of the pure solvent which makes it an accurate differential method is described in great detail by Jones and Ray, *J. Am. Chem. Soc.*, **59**, 187 (1937).

[1] *Wied. Ann.*, **17**, 361 (1882).

[2] *J. Am. Chem. Soc.*, **37**, 1643 (1915).

[3] *Ibid.*, **43**, 827 (1921); **46**, 1196 (1924).

[4] *Ibid.*, **41**, 499 (1919).

[5] *J. Chem. Soc.*, **119**, 1483 (1921).

[6] *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **23**, 49 (1933). See also Sutton, *Proc. Phys. Soc. London*, **45**, 88 (1933).

[7] *Manc. Memoirs*, **65** (1921), No. 5; *Trans. Faraday Soc.*, **17**, 384 (1922). See De Witt *et al*, *J. Am. Chem. Soc.*, **57**, 796 (1935).

[8] *J. Chem. Soc.*, **127**, 744 (1925).

[9] *Proc. Phys. Soc. London*, **41**, 214 (1929).

[10] *Proc. Ind. Assocn. Cultivation Sci.*, **9**, 155 (1925).

[11] *J. Chem. Soc.*, **135**, 1449 (1933). Cf. Natelson, U.S. 2,054,438 (1936).

required to depress the meniscus to the same arbitrarily selected level in each, successively. The following account of the method, which is also able to measure interfacial tension,[1] is reproduced from the author's paper.

Measurements were made in the apparatus *T* (see Fig. 92), which could be immersed in a glass trough of water for purposes of temperature control. *F* and *W* are the capillary tubes, and in the particular instruments used these were about 22 cm. long and had internal radii of about 0·02 and 0·06 cm. respectively. Some 5 c.c. of liquid were placed in the apparatus before it was connected as shown in the diagram. Suction was applied at *A* by means of a water aspirator designed so as to allow either rapid or slow action. The pressure, P_1, needed to force the meniscus in the wider capillary (*W*) down to some arbitrary level, was measured on the manometer (*M*), the meniscus being adjusted so that its convex edge coincided with the eye-piece marking of a low-powered travelling microscope and being illuminated from behind. The microscope, which had been levelled by use of a spirit level, was then turned on the other capillary (*F*), and the pressure, P_2, needed to bring the second meniscus to the eye-piece marking also observed. The difference, $P_2 - P_1 = \Delta P$ was a measure of the tension as will be shown.

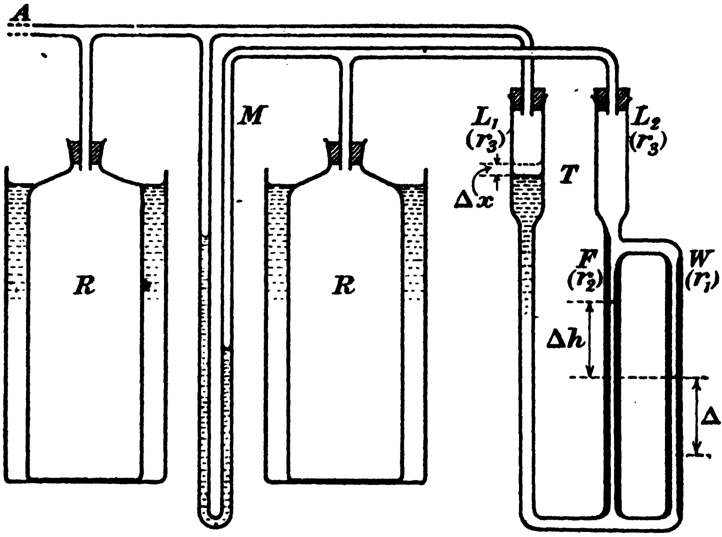

FIG. 92. Speakman's apparatus for determining surface tension and interfacial tension.

It was imperative to connect both sides of the apparatus *T* to the manometer as shown; if this were not done the menisci were very unsteady, in particular being disturbed by any sharp sound (presumably on account of the compression in the sound wave). It was also desirable to increase the capacity of the system by adding the reservoirs *R*, and these were water-jacketed.

Absolute alcohol was originally used as manometric liquid, following the practice of many previous workers. It was, however, found to be highly unsuitable; it is hygroscopic and the absorption of water is accompanied by a serious increase of density (1 or 2 per cent. during a month, for instance). *cyclo*Hexane was substituted for alcohol and found to be satisfactory, the choice being made because this liquid is stable in this respect and has as low a density as alcohol.

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[1] Cf. Bartell and Miller, *J. Am. Chem. Soc.*, **54**, 1961 (1928).

CALCULATION OF RESULTS

The derivation of surface or interfacial tensions from the values of ΔP permits of a high degree of precision. The contact angle must be zero (or be exactly known), a limitation which, however, necessarily applies to all similar methods of measuring surface tensions. It being assumed for the moment that the menisci in the capillaries are hemispherical, then if p_1 and p_2 are the pressure differences existing there on account of the curvature of the surfaces, and if r_1 and r_2 are the internal radii, in *W* and *F* respectively, it follows that

$$p_1 = 2\sigma/r_1 \text{ and } p_2 = 2\sigma/r_2 . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

Between the determinations of P_1 and P_2, as consideration of the figure will show, the liquid as a whole moves downwards in the capillaries by an amount Δh and upwards in L_1 by an amount Δx. These quantities are determined by the following equations:

$$\Delta h = (p_2 - p^1)/dg \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

from considerations of hydrostatic pressure, *d* being the density of the liquid, and

$$\Delta x \,.\, \pi r_3^2 = \Delta h \,.\, \pi(r_1^2 + r_2^2) \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

provided the tubes may be assumed to have uniform bores. Finally, we have

$$P_1 = p_1 + K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$\text{and } P_2 = p_2 + K + \Delta x \,.\, dg \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

K being a constant for any single pair of observations. Subtracting (4) from (5), substituting from (1), (2) and (3), and simplifying, we have

$$P_2 - P_1 = \Delta P = (p_2 - p_1)\left\{1 + \frac{r_1^2 + r_2^2}{r_3^2}\right\}$$

$$\text{whence} \qquad \sigma = \Delta P \Big/ 2\left\{1 + \frac{r_1^2 + r_2^2}{r_3^2}\right\}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad . \quad . \qquad (6)$$

$$\textit{i.e.,} \qquad \sigma = C.\Delta P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

C is determined by calibration with a liquid of known surface tension.

It will be noticed that the r_1 and r_2 occurring in the term $1/r_2 - 1/r_1$ of equation (6) are not strictly the same quantities as those in the other term in the denominator; the former refer to a particular level of the apparatus, whilst the latter are average values. Since, however, the term in which the latter occur differs only slightly from unity, no appreciable error is introduced by assuming them to be the same (*i.e.*, by assuming for the purpose of equation (3) that the tubes are uniform).

Allowance is necessary for the departure of the meniscus from the truly hemispherical form. Sugden's tables [1] permit exact computation. If, in equations (1), and in the terms of (6) and (8) derived from (1), r_1 and r_2 are replaced by b_1 and b_2, which are defined as the radii of curvature of the surfaces at the poles of the menisci, then these equations become rigidly true. Sugden's table gives the value of r/b when r/a^2 is known. So, for example, an approximate value of σ may be obtained from equation (6) and thence one of a^2. From this are calculated in turn r/a, r/b (from the table), and a more exact value of σ, the process being repeated if need be until a constant value emerges, though in practice one such approximation is usually enough.[2]

Sufficient accuracy for most purposes is realised by using a simple empirical formula based on Sugden's tables :

$$\sigma = \mathrm{C}\phi \,.\, \Delta\mathrm{P}$$

where ϕ is a correction factor having the value $(1-0{\cdot}3\, r_1 r_2/a^2)$ for radii of the order of those used and where C is the constant of equation (7).

A variation of the capillary rise method enabling the accurate determination of the surface tension of liquids has been proposed by Ferguson and Kennedy.[3] The capillary is used in a horizontal position to obviate determination of the density and thus permits a measurement with 1 or 2 c.c. of liquid without loss of precision. The contact angle is made zero by applying pressure until the meniscus is exactly plane, as observed with a microscope. For tubes of less than 1 mm. bore, the formula employed is $\sigma = \dfrac{rhdg}{2}$, where h and d refer to the manometer liquid. The manometer can be made direct reading. The advantages of the Ferguson-Dowson pressure method are gained, and it can be made direct reading like the original method.

Still another variation of the capillary tube method has been described by Achmatov.[4] It is known that a liquid drop in a conical tube will not remain in equilibrium. Using the Laplace equation, the pressure difference can be found under which the drop moves. On the side of the greater meniscus, $p_1 = \dfrac{2\sigma \cos \beta}{\mathrm{R}}$, and on the side of the smaller meniscus $p_2 = \dfrac{2\sigma \cos \beta}{r}$, where σ = surface tension, β = the angle of contact, and R and r = the radii of the capillary tube in the observed position of the menisci. The determined excess pressure is : $p = 2\sigma\left(\dfrac{1}{r} - \dfrac{1}{\mathrm{R}}\right)\cos \beta$. For complete wetting of the tube by the liquid, cos = 1 and, therefore, $p = 2\sigma\left(\dfrac{1}{r} - \dfrac{1}{\mathrm{R}}\right)$. Hence, knowing R and r, one can determine σ. With water at 18° C. in a capillary tube when R = 0·1 cm. and r = 0·05 cm., p = 1,500 dynes/cm.

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[1] *J. Chem. Soc.*, **119**, 1483 (1921).

[2] In accordance with common practice the capillary constant is defined by the equation $a^2 = 2\sigma/(d_2 - d_1)g$, d_2 and d_1 being the densities of the phases at equilibrium. Some authors, however, including Rayleigh and Ferguson and Dowson, use an a^2 which has half this value.

[3] *Proc. Phys. Soc. London*, **44**, 511 (1932).

[4] *Kolloid-Z.*, **66**, 266 (1934) ; see also Smith and Foote, *Ind. Eng. Chem.*, **21**, 567 (1929) on " Capillary Phenomena in Non-Circular Cylindrical Tubes."

Instead of a conical tube, the author uses two tubes of different diameter joined together, whence R and r are the radii of the tubes. Then $p = k\sigma$, where $k = \frac{1}{r} - \frac{1}{R}$, and is a constant for the apparatus, determined by using a liquid of known surface tension. The method gave good results for ethyl alcohol, chloroform, toluene and water. By inclining the apparatus until no movement of the liquid occurred, and measuring the angle of inclination, the pressure could be calculated from the horizontal component of the liquid weight.

An accurate method for the determination of surface tension when only a small quantity of liquid is available is obviously desirable. Kiplinger[1] used an inclined capillary tube, whilst Ferguson[2] suspended a short column of liquid in a vertical capillary tube and adjusted the pressure upon the top of the column until the lower surface became plane. A micro method, proposed by Mouquin and Natelson,[3] has wide application, with excellent accuracy. Even with only one drop of liquid the determination[4] is easily possible, with values which can be checked to 0·1 dyne/cm.

The method is somewhat comparable to that of Achmatov, already described. Working on the principle that a definite pressure is needed to move a short column of liquid along a tube of conical bore in the direction of the larger cross section, when the angle of contact is less than 90°, the authors found it most convenient to have a constant difference in terminal radii. At equilibrium, the external pressure is directly proportional to the surface tension. To secure a capillary with a small bulb-shaped enlargement (see Fig. 93), a broken thermometer stem was used, the capillary having an internal diameter of 0·0229 cm. Wherever the meniscus A is situated, its radius of curvature is constant while in the cylindrical portion of the capillary, so that all that is required is to move meniscus B to some arbitrarily selected position and note the pressure required. Plotting pressure against surface tension gives a straight line.

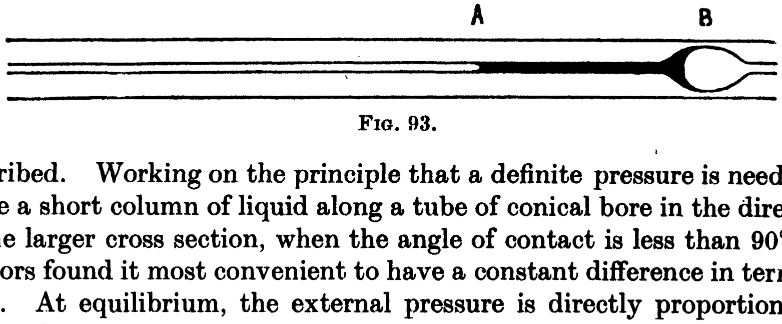

FIG. 93.

In the case of liquids which do not wet glass, notably mercury, immersion of a glass capillary tube in the bulk liquid causes a depression of the meniscus. Thus, Klemenc and Bankowski[5] measured the capillary depression of mercury by light interference, using the Michelson interferometer. For a tube width of 30 mm. the depression was 0·002 mm., and for width 40 mm. it was less than 0·0002 mm. An extensive investigation of the capillary depressions of mercury in cylindrical tubes has recently been published by Cawood and Patterson.[1]

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[1] *J. Am. Chem. Soc.*, **42,** 472 (1920).
[2] *Proc. Phys. Soc. London*, **36,** 37 (1923).
[3] *J. Phys. Chem.*, **35,** 1931 (1931).
[4] A later development is by Natelson and Pearl, *J. Am. Chem. Soc.*, **57,** 1520 (1935)
[5] *Naturwissenschaften*, **22,** 10 (1934).

Instead of a capillary tube, parallel plates have been used by several workers recently. Schultze [2] described a precision apparatus for setting the plates parallel. The thickness of the plates is an important factor which has been examined by Srivastava [3] and by Ray,[4] who derived an exponential equation to account for the discrepancies. Sata and Kurano [5] found that the theoretical curves are approached as the plate thickness increases. Apparently the composition of the plate is without influence.

The capillary rise method has been examined by many workers,[6] but attention is specially directed to an important paper by Jones and Frizzell.[7] Colloidal solutions present difficulties with this method, but the sessile drop method [8] is stated to have yielded reproducible and accurate results with paraffin chain colloidal electrolytes.[9]

DU NOÜY TENSIOMETER

This method is based on the familiar principle of tearing a metal ring from the surface of a liquid. A platinum-iridium ring of mean perimeter 4 cm. ± 0·005 cm. is made of wire of diameter 0·3 mm. This is suspended on an arm rigidly fixed to a fine steel piano wire (diam., 0·25 mm.), secured at both ends in torsion heads, each of which is driven by a worm-gear arrangement. Fig. 94 illustrates the complete apparatus.[10] A small quantity of the liquid to be examined is placed in a perfectly clean glass dish standing on the adjustable support. The ring is wetted with the liquid and the arm K then adjusted to its zero balance. The ring is then drawn into the liquid by raising the support Z until the surface of the liquid just touches the ring. The head A is now turned so as to move the vernier up scale and the micrometer adjusting screw B is turned with the left hand so as to lower the vessel containing the liquid. The arm K must always remain in the zero-balance position.[11] Slow and careful turning of the screws A and B finally bring about the sudden rupture of the ring from the liquid surface. The reading on the dial at this moment gives the surface tension directly in dynes/cm., expressed 0·1 dyne/cm. "Measurements made by untrained assistants were always found to agree to within 0·2 dyne."

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[1] *Trans. Faraday Soc.*, **29**, 514 (1933).

[2] *Kolloid-Z.*, **57**, 284 (1931); **60**, 132 (1932).

[3] *Ibid.*, **56**, 45 (1931).

[4] *Ibid.*, **59**, 280 (1932).

[5] *Ibid.*, **65**, 191 (1933).

[6] For example, Bounell, Byman and Keyes, *Ind. Eng. Chem.*, **32**, 532 (1940); Butler and Lees, *J. Chem. Soc.*, 1932, 2097; Cohan and Meyer, *J. Am. Chem. Soc.*, **62**, 2715 (1940); Dodd, *Phys. Rev.*, **48**, 487 (1935); Katz and Saltman, *Ind. Eng. Chem.*, **31**, 91 (1939); Kosakevich, *Z. physik. Chem.*, **133**, 1 (1928); Mahajan, *J. Sci. Instruments*, **13**, 189 (1936); Neros and Eversole, *J. Phys. Chem.*, **45**, 388 (1941); Quinn and Wernimont, *J. Am. Chem. Soc.*, **52**, 2723 (1930); Shereshefsky, *J. Am. Chem. Soc.*, **50**, 2966 (1928); Ubbelhode, *Ind. Eng. Chem., Anal. Ed.*, **9**, 85 (1937); Washburn and Berry, *J. Am. Chem. Soc.*, **57**, 975 (1935).

[7] *J. Chem. Phys.*, **8**, 986 (1940).

[8] Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938); Nutting and Long, *J. Am. Chem. Soc.*, **63**, 84 (1941); Porter, *Phil. Mag.*, **15**, 163 (1933); **24**, 823 (1937); **25**, 752 (1938); Tartar, Sivertz and Reitmeier, *J. Am. Chem. Soc.*, **62**, 2375 (1940).

[9] Tartar, Sivertz and Reitmeier, *loc. cit.*

[10] *Vide* Du Noüy, "Surface Equilibria of Biological and Organic Colloids" (New York, 1926), p. 24. The method is examined or used by: Alexander, *Trans. Faraday Soc.*, **37**, 15 (1941); Nutting, Long and Harkins, *J. Am. Chem. Soc.*, **62**, 1496 (1940); Macy, *J. Chem. Education*, **12**, 573 (1935); Lottermoser *et al.*, *Kolloid-Z.*, **63**, 295 (1933); **64**, 44 (1933); **66**, 276 (1934); **73**, 155 and 276 (1935).

[11] Klopsteg, *Science*, **60**, 319 (1924).

The method is useful for technical laboratories. Quite small amounts of liquid will suffice for tests (1 c.c.), and the time required for a complete determination need not exceed 30 seconds.

Critical attention has been given to the ring method by several prominent workers.[1] Dorsey [2] points out that when a ring is slowly raised from a sufficient surface of liquid which wets the ring, the resultant downward pull of the liquid passes through a definite maximum, and, in the case of a ring not too small, the pull reaches a lower and constant value prior to rupturing. The difference between the maximum and the constant pull is less as the thickness of the ring is reduced. "The surface tension may be derived from either of these values of the pull, but the procedures differ. As the maximum pull is the least that will suffice to detach the ring from the liquid, the method based on it may be called the ring detachment method. The lower and constant pull, observed

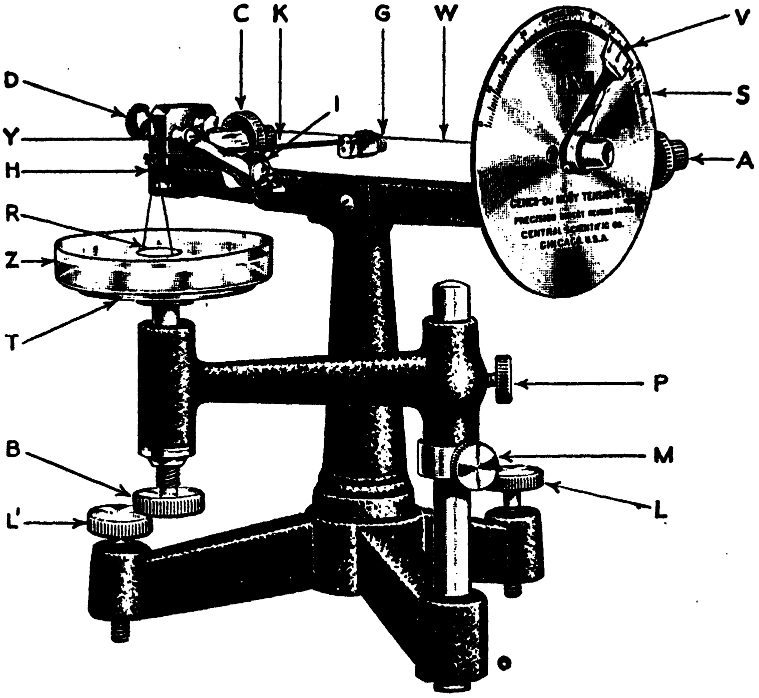

FIG. 94. The Du Noüy tensiometer.

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[1] MacDougall, *ibid.*, **62**, 291 (1925); Harkins, Young and Chen, *ibid.*, **64**, 333 (1926); Johlin, *ibid.*, **64**, 93 (1926); Schwenker, *Ann. Physik.*, **11**, 525 (1931).

[2] *Science*, **69**, 187 (1929). Rice, *J. Phys. Chem.*, **31**, 207 (1927), points out that the ring method does not give the static surface tension, but measures the "degree of staticness." See also Orbán and Reiner, *Biochem. Z.*, **211**, 487 (1929), for a discussion on the sources of error.

when the ring is raised sufficiently higher than the position of maximum pull, corresponds to the existence of a true double film between the liquid and the ring, and the method based on it may be called the ring film method. In the detachment method, a portion of the pull arises from the suction exerted by the column of liquid, in bulk, pendent from the ring and extending from it to the main body of the liquid. In the film method, a portion of this column has been replaced by the film, and only the weight of the small portion lying above the top of the film contributes to the pull, the rest of the pull being due to the film itself."

Dorsey refers to the confusion in the literature, some workers regarding the method as a detachment one and others as a film one. He believes that the film method is the one most frequently realised.

The effect of the size of the ring on the results given by the ring method has been discussed by several authors. Whilst it has been held that the method is independent of the angle of contact, Nietz and Lambert[1] have proved definitely that a relation exists between the pull on the ring and the angle of contact between the material of the ring and the liquid. The form of the function showing this relationship was ascertained to be :

$$F = 2l\sigma(1 + \cos\theta)^n$$

where F = force in dynes required to pull out the ring,
l = average perimeter of the ring,
σ = surface tension,
θ = angle of contact,
$$n = \frac{13{\cdot}1 \times \text{size of the wire}}{l} = 0{\cdot}227.$$

The function, however, did not hold over the entire range of wire sizes.

An exceptionally thorough study of the ring method has been made in Harkins' laboratory.[2] The experimental technique required in accordance with rigorous theory is detailed. Should the plane of the ring not be horizontal, the error introduced thereby is proportional to the square of the angle of tilt when this angle is small. An angle of 0·4° causes an error of 0·1 per cent., and 1° causes an error of 0·45 per cent. It is shown that the vessel which holds the liquid being tested must possess a diameter not less than 8 cm. The importance of the illumination employed is also stressed. " A necessary condition of the ring method is that the angle of contact between the ring and the liquid be zero." It was concluded that " as the ring is pulled out of the liquid the pull on it increases to a maximum and then decreases." However, it was found that only the maximum pull was measured with the technique employed. Freud and Freud,[3] in a communication from Harkins' laboratory, have studied in detail the theory of the ring method, based on the fundamental Laplace equation describing stable liquid surfaces. The equation was integrated numerically, giving data describing the shapes of the surfaces formed by raising a wetted ring out of a liquid. The authors present the data by a graph of two families of curves, from which it is possible to find certain ratios which are analogous to the dimensions of any particular ring and to the volume of any liquid held up by it. Their curves agreed with the experimental results, and the conclusion is reached that " the ring method may be considered an absolute one for the determination of surface tension."

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[1] *J. Phys. Chem.*, **33**, 1460 (1929).
[2] Harkins and Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930). See *ibid.*, **62**, 1496 (1940).
[3] *J. Am. Chem. Soc.*, **52**, 1772 (1930).

An appropriate example of the use of the ring method in technical work is afforded by Francis and Bennett[1] in a paper on " The Surface Tension of Petroleum." Attention must also be directed to the later development by DeGray[2] of a direct-reading surface tension balance, and the method described by Fahrenwald,[3] who replaces the ring by a very thin metal knife edge. The pull of a film of liquid is measured and very accurate results have been obtained. Fahrenwald has made thousands of surface tension measurements in connection with flotation work, and states : " it has been found that with oil-water emulsions it is the only instrument that will give true static[4] surface tension, *i.e.*, surface tension at the point where equilibrium between surface concentration and interior concentration exists. Most other methods measure the surface tension of relatively fresh surfaces and for emulsions give values from 1—15 dynes higher than that at equilibrium."

THE DROP-WEIGHT METHOD

This method has received detailed attention in recent years,[5] and holds high place for accuracy.

In 1864 Tate[6] observed that the weight of a drop of a liquid slowly detached from a vertical cylindrical tube is proportional to the radius of the tip of the tube. Worthington[7] gave the equation :

$$\mathrm{M}g = \pi r\sigma$$

for the maximum weight of a drop suspended in equilibrium from a tube. Much confusion has arisen over this point. Although the equation of Worthington is fundamentally sound,[8] many experimenters use the relation:

$$\mathrm{M}g = 2\pi r\sigma,$$

and Harkins regards this as the weight of an ideal drop.[9] Rayleigh[10] showed that the equation, $\mathrm{M}g = \pi r\sigma$, is more correctly expressed :

$$\mathrm{M}g = r\sigma\mathrm{F}\left(\frac{\sigma}{gdr^2}\right)$$

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[1] *Ind. Eng. Chem.*, **14**, 626 (1922) ; cf. Harvey, *ibid.*, **17**, 85 (1925).

[2] *Ind. Eng. Chem., Anal. Edn.*, **5**, 70 (1933). See also Hughes, *Trans. Inst. Rubber Ind.*, **8**, 473 (1933).

[3] *J. Optical Soc. Am.*, **6**, 722 (1922) ; cf. Wellman and Tartar, *J. Phys. Chem.*, **34**, 403 (1930). The use of a plate is described by Hughes, *Trans. Inst. Rubber Ind.*, **8**, 473 (1933), and Dognon and Abribat, *Compt. rend. soc. biol.*, **130**, 1000 (1939).

[4] Cf. the interesting paper by Rice, *J. Phys. Chem.*, **31**, 207 (1927), dealing with the " degree of staticness."

[5] Perrot, *J. chim. phys.*, **15**, 164 (1917) ; Michelli, *Phil. Mag.*, **3**, 581 (1927) ; Palitzsch, *Z. physik. Chem.*, **Abt. A. 138**, 399 (1928) ; Iredale, *Z. physik. Chem.*, **144**, 158 (1929) comments on the paper by Palitzsch ; Ferguson, *J. Sci. Instruments*, **6**, 163 (1929) ; Dauvé, *Bull. biol. pharm.*, **1934**, 131 ; Mohr and Moos, *Milchwirtschaft. Forsch.*, **15**, 261 (1933).

[6] *Phil. Mag.* (4), **27**, 176 (1864).

[7] *Proc. Roy. Soc.*, **32**, 362 (1881).

[8] Bouasse " Capillarité " (Paris, 1924), p. 264 ; Ferguson, *Brit. Assocn. Coll. Repts.*, **5**, 1—13 (1923) ; *Manc. Memoirs*, **65**, No. 4 (1921).

[9] Alexander's " Colloid Chemistry " (N.Y., 1926), Vol. I., p. 256. Also, Iredale, *Phil. Mag.*, **45**, 1088 (1923).

[10] *Phil. Mag.*, **48**, 321 (1899).

F being an arbitrary function. Lohnstein's work[1] led him to the equation:

$$Mg = 2\pi r\sigma F\left(\frac{r}{a}\right),$$

where $a = \sqrt{\frac{2\sigma}{d}}$. A table was given for $F\left(\frac{r}{a}\right)$, and in the range of values $\frac{r}{a}$ usual in experimental work, $F\left(\frac{r}{a}\right)$ is approximately constant, viz., about 0·62.

Harkins and Brown[2] have extended Lohnstein's investigations. They consider Tate's law ($W = Mg = 2\pi r\sigma$) is insufficient,[3] since the weight of a drop is also a function of the shape of the drop. The shape depends on the ratio between two linear dimensions of the drop r and l. A drop does not become detached from a tip from its exact edge, but forms a neck a little below the edge and then detaches.[4] Its weight, therefore, is less than the "ideal" weight. Harkins proceeds: "since r is a linear dimension of any hanging drop, it is evident that if l is some other linear dimension of the drop, $\frac{r}{l}$ will remain constant if the form of the hanging drop is kept constant while its volume is changed. In place of l the cube root of the volume of the drop, $V^{\frac{1}{3}}$, may be taken. Now if the form of the hanging drop determines what fraction of it will fall, then the actual weight of the falling drop is:

$$\begin{aligned} W &= 2\pi r\sigma . F\left(\frac{r}{l}\right) \\ &= 2\pi r\sigma . F(^r/_{V^{\frac{1}{3}}}). \end{aligned}$$

The square root of the capillary constant is a, and this acts as a linear dimension of the drop, whence:

$$W = 2\pi r\sigma . F'\left(\frac{r}{a}\right).$$

Since $$W = mg.$$

$$\begin{aligned} \sigma &= \frac{mg}{2\pi r F\,(^r/_{V^{\frac{1}{3}}})}. \\ &= \frac{mg}{2\pi r F'\,(^r/_a)}. \\ &= \frac{mg\phi}{2\pi r}. \end{aligned}$$

The authors furnish[5] a table of drop-weight surface tension corrections, connecting $^r/_{V^{\frac{1}{3}}}$ with $F\,(^r/_{V^{\frac{1}{3}}})$. For single liquids, the capillary tips should be chosen so that $^r/_{V^{\frac{1}{3}}}$ lies between 0·759 and 0·95.

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[1] Freundlich, "Colloid and Capillary Chemistry," p. 21.

[2] *J. Am. Chem. Soc.*, **38**, 228 (1916). Summarised by Harkins in Alexander's "Colloid Chemistry," Vol. 1, 256.

[3] Correct results are given with this equation, since *comparisons* only are made.

[4] For mathematical analysis, cf. Bouasse "Capillarité," p. 264.

[5] *J. Am. Chem. Soc.*, **41**, 499 (1919).

The simple determination of the surface tension of a liquid is made thus.[1] The mass of one drop of the liquid is determined, and its volume (V) then calculated (its density being known). Evaluating $V^{\frac{1}{3}}$ and looking in the tables for F will enable the calculation of $\frac{mg}{2\pi r\text{F}}$.

Freud and Harkins[2] have pointed out that the Harkins-Brown method is purely empirical in regard to the relations between the size of the drop and the known constants of liquid and tip. Accordingly, they endeavoured to supply a theoretical basis for the empirical relations, studying the changes occurring when a drop of liquid falls from a circular horizontal tip. Whilst the theory of the *hanging* drop is fairly well worked out, the information regarding the *detached* drop is empirical,[3] and practically no rigid theory is available regarding the *detaching* drop. Their paper, containing many calculations and curves, concludes with highly interesting profiles of hanging and detached drops taken by a motion picture camera.

A further study by Gans and Harkins[4] concerned the effect of an inclination of the tip upon the drop weight, whence it was concluded that "the effect upon the weight of a drop of a tilt of the tip of less than 3° is not appreciable."

A full description of a simple apparatus for accurate and rapid determination of surface tension by this method is given by Harkins and Brown.[5] The speed of formation of a drop is an important factor. Thus the authors found when dropping water from a glass tip of radius 0·24456 cm., that the drop weight rises rapidly if the time of formation is faster than one drop in three minutes.[6]

Recently Hauser and co-workers[7] have published extraordinarily interesting accounts, with excellent illustrations, of the application of the high-speed cine-camera to research on the surface tension of liquids. The successive steps in the formation of drops and in the mechanism of the tearing-ring are outlined. For example, a series of high-speed motion pictures of the ring method were taken at a speed of 600 exposures per second, using distilled water, water containing triethanolamine oleate as a capillary-active substance, and glycerol. The authors conclude: "The stroboscopic analysis of the phenomena appearing in connection with surface tension measurements by the drop-fall and the ring method show motions of such a high degree of complexity as to suggest that neither of these methods is ideal from the standpoint of accurately determining surface tension. To obtain comparable data with solutions of capillary-active substances it seems indispensable to indicate the time of drop formation or rest period of the liquid surface when determining surface tension with the methods discussed."

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[1] *Loc. cit.*, p. 520. For practical examples see Gibby and Addison, *J. Chem. Soc.*, **1936**, 126; Gibby and Argument, *ibid.*, **1940**, 600. See also an important note by Bailey, *Nature*, **137**, 323 (1936), concerning the influence of gravity.

[2] *J. Phys. Chem.*, **33**, 1217 (1929); cf. Porter, *Phil. Mag.*, **8**, 180 (1929), on "The Mechanics of Drops Pendent from Cylindrical Tubes"; Adler, *Physik. Z.*, **35**, 864 (1934), deals with drop weight as a function of the dropping velocity and of the diameter of the drainer.

[3] Cf. Neumann and Seeliger, *Z. Physik.*, **114**, 571 (1939).

[4] *J. Am. Chem. Soc.*, **52**, 2287 (1930).

[5] *Ibid.*, **38**, 246 (1916).

[6] See Zunz in Alexander's "Colloid Chemistry," Vol. 2 (New York, 1928), p. 651.

[7] Hauser, Edgerton, Holt and Cox, *J. Phys. Chem.*, **40**, 973 (1936), and Edgerton, Hauser and Tucker, *ibid.*, **41**, 1017 (1937). Duch, *Compt. rend.*, **203**, 1336 (1936), deals with the determination of surface tension by formation of drops at the bottom of a capillary tube by observation of the elongation of the meniscus.

BOUNDARY TENSION BY PENDANT DROPS

The most recent development of a method for measuring surface tension is that by Hauser and his co-workers,[1] who modernised the old method of the pendant drop. They suspend a small drop of the test liquid from the end of a vertical tube mounted in a thermostat. The surface of the drop is a surface of revolution whose shape and size can be determined by measurements made on a large photographic image obtained with a special camera built for this purpose. Since the equations determining the equilibrium of the drop are known, the boundary tension of the liquid can be calculated from a few simple measurements made on a photograph of a hanging drop. The method is stated to be accurate to ± 0·05 per cent. " Future improvement depends upon a more precise determination of the mathematical function connecting drop shape with boundary tension and upon the construction of special, high-precision equipment." The accuracy of the method has been demonstrated by Smith and Sorg [2] using benzene, toluene, carbon tetrachloride and water. Surface tension data were secured for the normal aliphatic alcohols from methyl alcohol to lauryl alcohol and for all of the readily obtainable isomers below hexyl alcohol.

A variety of other methods are available for determining surface tension, such as the ripple method,[3] stationary waves on a vertical jet,[4] and the maximum bubble method.[5] For viscous liquids Pfund and Greenfield [6] recommend a method where a small jet of air impinges on the surface of the liquid producing a small depression whose depth is an inverse function of the surface tension.

INTERFACIAL TENSION

Du Noüy's Tensiometer. A simple method for determining the dynamic and static interfacial tension has been developed by Du Noüy, based on the tensiometer already described. The instrument (Fig. 95) is a modified tensiometer, enabling the platinum ring to be pressed down vertically, its plane remaining horizontal. The ring is attached to a rigid support maintained perpendicular. Movement of a vernier clockwise or counter-clockwise moves the ring down or up—down when water has the lower density of the two liquids investigated, up in the opposite case. Fig. 96 shows the appearance of the interface between water (upper layer) and carbon tetrachloride (lower layer) when the ring is pressed down, just prior to breaking.[1]

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[1] Andreas, Hauser and Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

[2] *Ibid.*, **45**, 671 (1941).

[3] Tyler, *Phil. Mag.*, **31**, 209 (1941).

[4] Satterly and Strachan, *Trans. Roy. Soc. Can.*, **29** (iii), 105 (1935).

[5] Baker and Gilbert, *J. Am. Chem. Soc.*, **62**, 2479 (1940); Belton, *Trans. Faraday Soc.*, **31**, 1413 (1935); **36**, 493 (1940); Bosworth, *ibid.*, **34**, 1501 (1938); Bradley, *J. Am. Chem. Ceram. Soc.*, **21**, 339 (1938); Brown, *Phil. Mag.*, **13**, 578 (1932); Butler and Wightman, *J. Chem. Soc.*, **1932**, 2089; Cassel, *J. Am. Chem. Soc.*, **57**, 2009 (1935); Haendler and McGuire, *J. Chem. Education*, **14**, 591 (1937); Trieschmann, *Z. physik. Chem.*, **B. 29**, 328 (1935).

[6] *Ind. Eng. Chem., Anal. Ed.*, **8**, 81 (1936).

The method is well adapted for studying the influence of temperature on the interfacial tension and for following adsorption in relation to time.

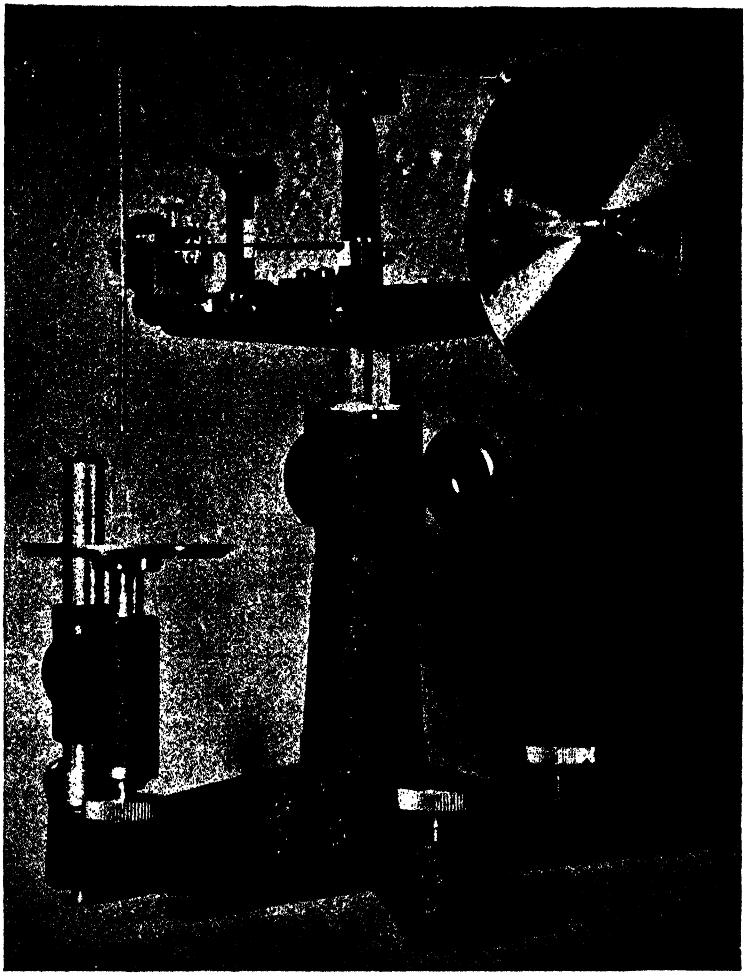

Fig. 95. Du Noüy's tensiometer for determining interfacial tension.

A similar method is a modification of Fahrenwald's, in this case using a knife-edge frame. It is stated to have furnished good results in technical practice.

Capillary Height Method. Harkins and Humphery[2] describe an apparatus which permits very accurate determination of the dineric interfacial tension. Consider the liquids water/benzene. A wide container holds water in which a vertical capillary is completely immersed. Benzene is poured on the water surface. A rachet enables the capillary tube to be raised until the water/benzene meniscus in the tube *falls* to a definite point (x) according to a scale. A fine platinum pointer is now adjusted to touch the main water/benzene interface (y). The distance between x and y is thus very accurately determined either by verniers on the millimetre scale or by a cathetometer. The equation : $\sigma = \frac{1}{2} rhg (d - d')$ still holds, where d = density of water, and d' = density of benzene. The densities require to be very accurately determined, and in this connection the inter-solubility of the liquids must be considered. Temperature control is essential.

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[1] Photographic recording of du Noüy tensiometer readings are described by: Merigoux and Aubry, *J. chim. phys.*, **36**, 221 (1939); Tillat and Aubry, *Compt. rend.*, **207**, 427 (1938).

[2] *J. Am. Chem. Soc.*, **38**, 239 (1916).

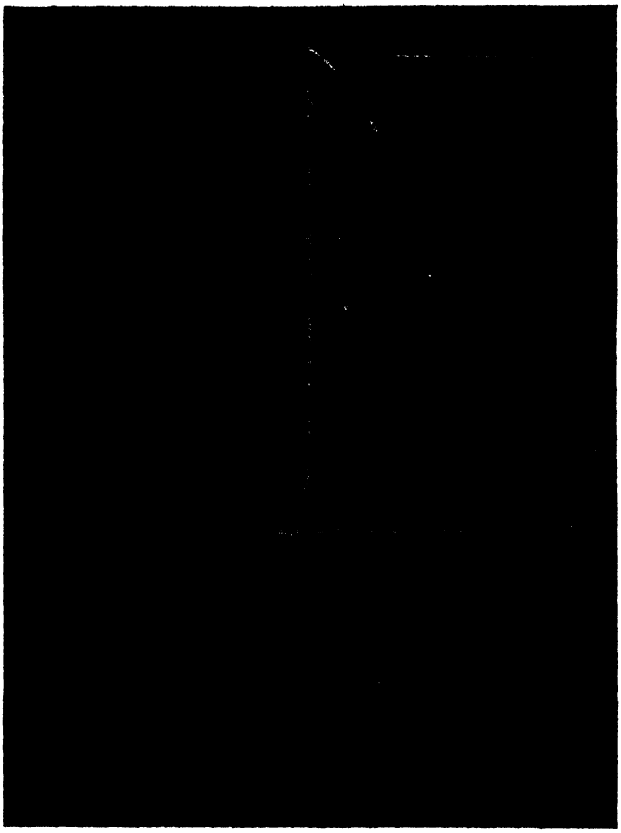

FIG. 96. The dineric interface.

Another method based on capillary rise has been proposed by Reynolds,[1] but has been adversely criticised by Ferguson.[2]

Speakman's method for surface tension determination has also been used for the determination of interfacial tension, the experimental procedure being similar. The interface was formed either above or below the capillaries, as the system demanded, so that the menisci could be drawn in the direction of their convexity. Sufficient of the two phases needed to be present for their free surfaces to lie in the limbs L_1 and L_2. If d_1 and d_2 are the densities (bulk) of the upper and the lower phase, a similar treatment to that given previously leads to the corresponding formula:

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[1] *J. Chem. Soc.*, **119**, 460, 466 (1921). Cf. Pound, *ibid.*, **123**, 578 (1923).
[2] *Brit. Assocn. Colloid Repts.*, **5**, 10 (1923).

$$\sigma_1 = \Delta P \Big/ 2\left\{1 + \frac{(r_1^2 + r_2^2)}{r_3^2} \cdot \frac{(d_2 + d_1)}{(d_2 - d_1)}\right\}\left(\frac{1}{r_2} - \frac{1}{r_1}\right).$$

When the densities approach equality, the term $(d_2 + d_1)/(d_2 - d_1)$ becomes large and the method inaccurate or even inapplicable; but the same is true of all known methods of measuring interfacial tensions.

Bartell and Miller[1] have described a method based upon the capillary tube principle and have designed two somewhat different types of apparatus giving satisfactory results. The method is rapid and can handle non-transparent liquids of any density. The principle of the apparatus is shown in Fig. 97 reproduced from the authors' paper. The apparatus consists of a glass cup, A, about 4 cm. in diameter and 8 cm. in depth to the bottom of which is sealed a capillary tube outlet of about 0·3 mm. radius. The remainder of the apparatus consists only of an open dish, B, which is large enough to eliminate effects due to capillarity.

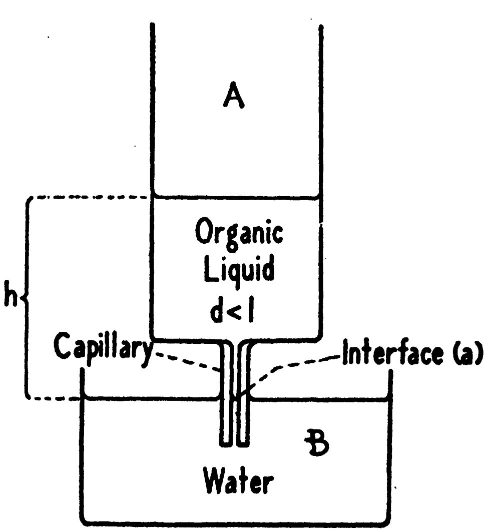

Fig. 97. Bartell and Miller's method for determining interfacial tension.

To determine interfacial tension, the capillary is immersed in the dish of water, B, until the calibration mark a is exactly level with the surface. Water rises in the capillary to the bottom of the cup and so wets the capillary throughout its length. The organic liquid is now slowly added from a burette, eventually by drops, until the water/organic liquid boundary is forced downward to the mark a. By means of a cathetometer the height of the organic liquid is measured. If d = the density of the organic liquid, the interfacial tension, $\sigma_{2,3}$, is calculated from the equation:

$$\sigma_{2,3} = \frac{rhdg}{2}.$$

The method has been employed by Bartell, Case and Brown,[2] to determine the interfacial tension of mercury with organic liquids.

Later, Mack and Bartell[3] described two new types of apparatus for securing accurate values of interfacial tensions, when only small amounts of the non-aqueous liquid are available. One type of apparatus permits good results without the necessity of careful determination of the density of the organic liquid, and the other yields very accurate results if the density is known or is determined with precision. The authors' paper should be consulted for details.

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[1] *J. Am. Chem. Soc.*, **50**, 1961 (1928).

[2] *Ibid.*, **55**, 2419 (1933).

[3] *Ibid.*, **54**, 936 (1932).

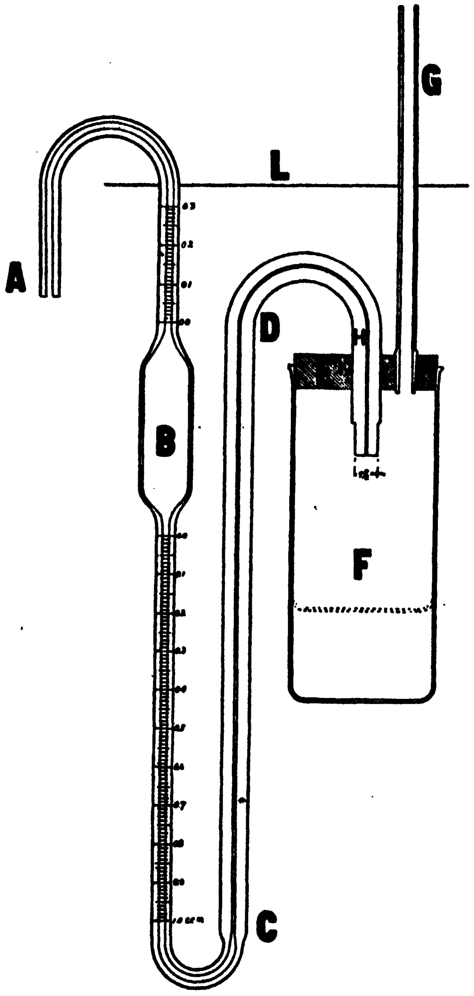

Fig. 98. Harkins and Humphery's apparatus for interfacial tension measurements.

The Drop-Weight Volume Method. This method was developed by Harkins and Humphery,[1] and enables rapid and accurate results to be made. Fig. 98 illustrates the apparatus. The pipette ABCD contains the aqueous phase. The tip dips beneath the liquid in F. The aqueous phase is now carefully brought to the exact end of the capillary tip and the meniscus in the tube immediately above the bulb B noted. By careful suction at G drops are detached at the tip and the meniscus falls to below the bulb B. The volume of a drop is thus evaluated. One may determine directly the volume of one drop and still obtain very accurate results. The interfacial tension is then calculated as follows:

$$\sigma = \frac{V(d - d')g}{2\pi r F\,(r/V^{\frac{1}{3}})}.$$
$$= \frac{V(d - d')g\phi}{2\pi r}.$$

where d and d' = densities of the liquids concerned.

The corrections involved are the same as those of the drop-weight method as given by Harkins and Brown.[2]

That liquid which wets the tip the better is the one to be expelled as drops; depending on the relative densities of the liquids, the face of the tip will be placed downward or, by bending the capillary, upward, the drops then falling or rising, as the case may be, through the other liquid.

Hartridge and Peters,[3] in an investigation on the effect of *p*H on certain interfacial tensions, employed a drop-pipette. A 1 c.c. pipette (graduated) was turned up at the lower end. Very accurate control was exercised over the quantity of liquid delivered during the formation of single drops, and over the time of formation and break-away of the drops. The equation

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[1] *Ibid.*, **38**, 236 (1916).

[2] *Ibid.*, **41**, 519 (1919). A very accurate modification is by Eversole and Dedrick, *J. Phys. Chem.*, **37**, 1205 (1933), and by Dedrick and Hanson, *ibid.*, **37**, 1215 (1933). See also: Evans, *Trans. Faraday Soc.*, **33**, 794 (1937), and Guest and Lewis, *Proc. Roy. Soc.*, A. **170**, 501 (1939).

[3] *Proc. Roy. Soc.*, A. **101**, 348 (1922).

$$\sigma_{AB} = \frac{b(D_B - D_A)g}{nrf}$$

was used, where

b = volume of drop in cubic centimetres.
D_B = density of aqueous layer.
D_A = density of benzene.
r = radius of tip.
f = empirical factor.
n = number of drops (taken as 1).

The value of rf was found by direct determination of the drop volume for the benzene/water interface with the apparatus. This interface value is accurately known.[1]

Practically all the earlier interfacial tension measurements in emulsion studies have been made by a modification of the drop-weight method.[2]

For a drop of liquid hanging from a capillary tube dipping into a second liquid there exists a balance between the weight of the drop and the surface forces supporting it.

If r = radius of the capillary tube,
d = density of the dropping liquid,
d' = density of the second liquid,
m = weight of the drop,
g = the gravity constant,

then the interfacial tension is given by the relation

$$\sigma = \frac{mg}{\pi r}\left(\frac{d - d'}{d}\right).$$

If a volume of liquid, V, falls steadily from the capillary tube into the second liquid, making a total of N drops, it follows that $\sigma \propto \frac{V}{N}$, *i.e.*, the interfacial tension, is inversely proportional to the number of drops. For two different liquids, *e.g.*, a vegetable oil and a mineral oil, the relative interfacial tensions against a third liquid, *e.g.*, water, will be inversely proportional to the drop numbers obtained.[3]

The method is only used for comparative purposes, and even then is open to objections.[4] For determining absolute tensions several corrections must be made, since the formula has been deduced by applying a statical theory to a dynamic phenomenon.[5] The detachment of a drop of liquid is a complex affair, and very varying effects may be introduced when pairs of different liquids are under examination.[1] Thus, Kiesel[2] finds that the weight of the drop is a parabolic function of the time of formation, due to adsorption of the surface-active substance on the enlarging surface of the drop.

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[1] Harkins and Humphery, *J. Am. Chem. Soc.*, **38**, 242 (1916).

[2] *Ibid.*

[3] Cf. Lewis, *Phil. Mag.*, **15**, 508 (1908); **16**, 467 (1909).

[4] *Vide* Ferguson, *Manchester Memoirs*, **55** (iv), 14 (1921).

[5] *Vide* Lunn, *J. Am. Chem. Soc.*, **41**, 620 (1919).

Since interfacial tension is inversely proportional to the number of drops, it follows that a decrease in this tension will be marked by an increase in the drop number ; in other words, a smaller tension supports a smaller weight, hence a given volume of liquid gives more drops. It will now be evident that if a liquid A flows as drops through a liquid B, and the interfacial tension can be reduced, the liquid A will yield a greater number of drops, corresponding to a greater dispersive capacity in liquid B. In other words, the tendency for A to become emulsified in B increases as the interfacial tension decreases. It is in this connection that the drop number furnishes useful data regarding the emulsifying capacities of liquids, though it must again be emphasised that in many cases the results may only be approximate comparisons.[3]

Donnan[4] and his pupils determined the drop numbers of various oils against water or aqueous solutions, using a pipette with a curved-up tip, so that the lighter liquid ascended in drops through the denser medium. The drop-pipette consists essentially of a pipette with a bulb whose capacity depends on the liquids under investigation, and may be from 5 c.c. to 40 c.c., between two fixed marks on the stem, E and E′. If the relative tensions of, say, oil against soap solutions be required, the pipette is filled with oil to the mark E by suction through a side arm, whose tap is then closed. The pipette is carefully wiped at the tip, and then immersed in the soap solution under test contained in a glass cylinder which is held in a thermostat at some fixed temperature. The level of the solution above the tip of the pipette is maintained the same in the whole series of determinations made. After the oil and solution have attained the temperature of the thermostat, the main tap is opened and air is very slowly admitted through a fine capillary tube sealed on to the stem of the pipette. Drops of oil should form very slowly—at about twelve seconds' interval—and rise through the solution, their number being carefully counted.

When drops of oil rise through a soap solution there occurs adsorption of soap at the oil/solution interface, and in consequence the interfacial tension is lower than in the case of oil/pure water. If, instead of soap solutions, other colloidal solutions be used, *e.g.*, gelatin, gums, proteins, etc., similar adsorption of the colloid takes place. It is in consequence of this adsorption with the resulting formation of a surface film or envelope[5] that there arises one of the limiting factors in the general application of the method. Clowes[6] affirms that "the drop method affords an accurate means of determining the exact effect exerted by given substances on the colloidal equilibrium of the interfacial film." This statement, however, needs qualification. In certain cases, the elasticity and strength of the films enveloping the rising drops allow the drops to expand and distort and be detachable from the pipette only with difficulty. Thus Briggs and Schmidt observed such disturbances when determining the drop numbers of benzene in aqueous solutions of gelatin and gum arabic. Their experience led them to the conclusion that "drop numbers are not a fair and sufficient test for an emulsifier in solution." In such cases drop-number determinations fail to give an accurate measure of the ability of the solution to emulsify oil or other disperse phase.

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[1] Cf. Kurtz, *ibid.*, **49**, 1991 (1927).

[2] *Deut. tierarztl. Wochschr.*, **32**, 697 (1924).

[3] Cf. Simm, *J. Soc. Dyers Colourists*, **42**, 212 (1926).

[4] *Z. physik. Chem.*, **31**, 42 (1899) ; *Brit. Med. J.*, Dec. 23 (1905) ; *Engineering*, **99**, 551 (1915).

[5] Cf. Harkins, *J. Am. Chem. Soc.*, **39**, 590 (1917) ; Junker, *Kolloid-Z.*, **52**, 231 (1930) Traube, *ibid.*, **53**, 300 (1930) ; Traube and Weber, *Biochem. Z.*, **219**, 468 (1930).

[6] *J. Phys. Chem.*, **20**, 407 (1916).

The drop method is interesting owing to the part it has played in the development of our present knowledge of emulsification and emulsions, but it should undoubtedly be replaced in future work by a method capable of greater accuracy.[1]

The Determination of Phases. It is frequently necessary in work on emulsions to determine which of the two liquid phases is the continuous and which is the dispersed phase. Since with oil and water two types of emulsion are possible, oil-in-water and water-in-oil, a ready and accurate means of differentiating between these types is very desirable. Particularly is this the case when studying the problem of the reversal of phases. Several methods have been proposed :—

(*a*) **The Indicator Method.** Robertson [2] suggested the use of an oil-soluble, water-insoluble dye, Sudan III. This red dye, as a finely-divided solid, is dusted on to the surface of the emulsion to be examined. If the oil phase be continuous, then the dye will gradually spread throughout the system owing to its dissolving in the oil. If, however, water or aqueous solution be the continuous phase, then the dye will not spread, being confined to those globules of oil with which it comes into immediate contact. This method is useful in dealing with solid systems like butter and margarine, which are to be examined under the microscope. Thus Palmer [3] used acetone solutions of Sudan III and fuschin to stain the butter-fat globules in cream, and was able to prove the inversion of phases on churning. For emulsions in general there are objections to the use of added organic substances which may exert a new influence on the system.[4]

Newman [5] used this method with emulsions of benzene and water, employing iodine and methyl orange, the former soluble in benzene, the latter soluble in the water phase. Hall [6] employed the indicator method for emulsions of water in various organic liquids, using the water-soluble dye Nilblau and the oil-soluble dyes Scharlach Roth (Grubler) and dimethyl-amidoazo-benzene (Merck).

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[1] Recent applications of the method: Canals and Ramahenina-Ranaivo, *J. pharm. chim.*, **16**, 431 (1932); Andreev, *Repts. Lubricating Oil Comm.* (U.S.S.R.), **3**, 28 (1933); Dubrisay, *Chimie et industrie*, Special No. (April, 1934), 200.

[2] *Kolloid-Z.*, **7**, 7 (1910); French, *Stain Tech.*, **1**, 79 (1926), finds Candle Scarlet (Geigy) and Oil Red O (Nat. Aniline) superior to Sudan III., whilst Proescher, *ibid.*, **2**, 60 (1927), recommends Oil Red O Pyridin. Umbelliferone is a fluorescent indicator useful for the titration of emulsions: Volmar, *Documentation sci.*, **5**, 33 (1936).

[3] Missouri Agr. Expt. Sta., *Bull.*, **163**, 40 (1919).

[4] Cf. Clowes, *J. Phys. Chem.*, **20**, 445 (1916).

[5] *J. Phys. Chem.*, **18**, 34 (1914).

[6] *Ibid.*, **21**, 616 (1917).

(*b*) **The Drop-dilution Method.** The principle of this method is that an emulsion can be diluted by addition of the external or continuous phase, but not by adding the dispersed phase. Pickering [1] first recognised the principle, pointing out that an emulsion containing 99 per cent. by volume of mineral oil in 1 per cent. soap solution " will mix perfectly with water to form a weaker emulsion, but will not mix with more paraffin."

Briggs [2] suggested that the phase relationships of an emulsion could be determined by placing a drop of emulsion in a little water, and stirring. If the emulsified particles spread in the water, then water is the external phase ; if no spreading occurs, then water is the internal phase.[3]

Newman [4] found this method much more reliable than the indicator method. Hall [5] proposed a modification of the test for not too opaque emulsions. A drop of one of the liquids is placed in the emulsion near to the glass wall of the container. If the liquid is the dispersed phase " it is clearly delimited and moves up or down through the emulsion." If it be the continuous phase, it rapidly diffuses into its surroundings, making a slightly less opaque area. In the case of emulsions of water in hydrocarbon oils, as obtained by Hall, water sinks as a clear drop, whereas oil rises and diffuses.

The drop-dilution test is not satisfactory when dual emulsions are formed, and Woodman [6] has recommended that the test be carried out both in water and in the oil phase concerned, preferably on the aged emulsion.

(*c*) **The Electrical Conductance Method.** This method, proposed by the writer,[7] is based upon the fact that an oil-in-water type of emulsion, particularly when the aqueous phase contains small quantities of electrolytes, will show an electrical conductivity, whilst water-in-oil emulsions, characterised by having oil—an electrical insulator—as the continuous phase, will not conduct electricity. Sherrick [8] used this method in his investigations of crude mineral oil emulsions containing water as the internal phase. Bhatnagar [9] has demonstrated the great utility of the electrical method, and found it to be very sensitive indeed. He examined his emulsions in a bottle fitted with two platinum electrodes fixed at a constant distance apart. The application of a constant voltage for a second or two produced a current (measured in milliamps.) with all emulsions of the oil-in-water type. Emulsions of the opposite type allowed only—if at all—a very small current of the order of 0·1 milliamp., as against currents of 10 to 13 milliamps. for the oil-in-water emulsions.

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[1] *J. Chem. Soc.*, **91**, 2002 (1907).

[2] *J. Phys. Chem.*, **18**, 34 (1914).

[3] *Vide* also Holmes and Cameron, *J. Am. Chem. Soc.*, **44**, 67 (1922).

[4] *J. Phys. Chem.*, **18**, 34 (1914).

[5] *Ibid.*, **21**, 617 (1917).

[6] *Chem. News*, **144**, 225 (1932) ; *J. Soc. Chem. Ind.*, **51**, 95 T. (1932). See also Goettsch, *Chem. Weekblad.*, **26**, 336 (1929).

[7] Clayton, *Brit. Assocn. Colloid Repts.*, **2**, 114 (1918).

[8] *Ind. Eng. Chem.*, **12**, 135 (1920).

[9] *J. Chem. Soc.*, **117**, 542 (1920).

The reversal point could thus be readily detected, and in all Bhatnagar's studies on emulsion reversals this method was used.

Pick [1] used the method to determine the emulsion-forming capacity of fats. Two copper plates were kept apart by two pieces of glass of about 2 mm. thickness. With emulsions at 40°—50° C., breaking was observed by the glowing of an electric lamp of 50 c.p. with alternating current of 120 volts and 50 cycles passing through the electrodes and the emulsions. Palmer [2] employed the conductivity method in his studies of the churning of cream into butter, finding that the resistance of the cream during churning rises to a maximum (see p. 430).

(*d*) **Refractive Index Method.** Carrière [3] devised a method based upon the same principle as the determination of *n* of minerals. The advantage of this method is the entire absence of changes in the emulsion. A parallel bundle of light passing through a drop of oil in water will be converged, since the refractive index of oil exceeds that of water. With a drop of water in oil the bundle will be diverged. Illuminating with a parallel bundle from the right, with oil in water will give a bundle of which the rays from the left will come into the objective and those from the right will be invisible. In the microscope there is seen an illuminated border on the right side of the drop, whereas the other side appears dark. A drop of water in oil will show the opposite phenomenon. Instead of producing a bundle from one side, there can be inserted a diaphragm in the shape of a half moon between the concave mirror and the condenser of the microscope.

Van der Burg [4] has drawn attention to the fact that a drop of greater refractivity than the dispersion medium acts as a positive, and under reversed conditions as a negative lens. The objective of a microscope is sharply focused upon the largest circumference of a globule of greater refractivity. On raising the objective slightly, the circle becomes indistinct, and the image of the light source appears within. With drops of lower refractivity the image is found below them.

(*e*) **Fluorescent Light Microscopy Method.** Frosch and Hauser [5] have pointed out the possibility of following emulsification with the aid of the fluorescent light microscope. Thus, if a drop of water which is non-fluorescent is contacted with a drop of oil in which is dissolved anthracene (strongly fluorescent), both on a u.v. transmitting slide, and the system is examined with the ultra-violet light microscope using transmitted light, only the drop of blue fluorescing oil is visible in the field. In the course of time minute crystals with a light greenish-blue fluorescence are seen in the oil drop adjacent to the oil/water interface.

Examinations were made of O/W and W/O emulsions using a solution of rosin in an asphalt-base crude oil (greenish-blue fluorescence). If 1 per cent. aqueous NaOH is stirred with this rosin solution, each oil drop is haloed with a strongly fluorescent blue ring, whereas if 1 per cent.

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[1] *Chem. obzor*, **3**, 199, 202 (1928); cf. Parke, *J. Chem. Soc.*, **1933**, 1113.
[2] *Colloid Symposium Monograph*, **1**, 411 (1923).
[3] *Chem. Weekblad.*, **26**, 413 (1929).
[4] *Chem. Weekblad.*, **28**, 251 (1931).
[5] *Ind. Eng. Chem., Anal. Edn.*, **8**, 423 (1936).

aqueous $CaCl_2$ is used, the blue rings are not seen around the dispersed water globules. This is because the continuous (oil) phase is homogeneously fluorescent (bluish-green), so obscuring the blue colour of the calcium resinate adsorbed on the surface of the water globules. Addition of a crystal of anthracene, which is oil-soluble, brings a fluorescent response only from the W/O emulsion.

SIZE-FREQUENCY ANALYSIS OF EMULSIONS

Size-frequency analysis or the determination of the statistical distribution of the size of dispersed particles in colloid systems is of considerable theoretical importance. Numerous investigations have been made and many methods employed.[1] It is only comparatively recently, however, that attention has been paid to the size-frequency analysis of emulsions, as it is now realised that a comprehensive theory of emulsions must embrace the quantitative facts of the size and number of the dispersed globules. Where homogenisation is not attempted, such analysis is fundamental to studies on the viscosity of emulsions, the different methods of preparing emulsions and the investigation of natural emulsions, such as milk or rubber latex.

The earlier experiments of Svedberg and Estrup[2] involved the size-frequency analysis of mercury sols, milk, etc. The method employed was the direct ultra-microscopic measurement of the rate of fall of a statistically sufficient number of globules, the emulsion being contained in a cell with parallel walls, illuminated by a dark field condenser. Later, mercury sols received detailed study by Nordlund.[3]

In the study of milk the question of the size-frequency analysis of the fat globules has engaged the attention of many workers. The very careful experiments of Campbell[4] may be cited in this connection. He combined a euscope (Bausch and Lomb) with a microscope so as to avoid the strain of continuous changing of focus which is so necessary in the measurement of the fat globules by direct microscopic observation, if the very small globules are not to be missed. His arrangement of apparatus projected the fat globules on a white opaque screen, thus greatly enlarging their appearance. A stage micrometer scale was projected on a white cardboard in front of the screen. A square field measuring 100 μ each side was marked off on this cardboard, rulings being made one way, with each space equivalent to 2 μ. " In making this scale the microscope was equipped with an oil immersion objective, a 10x ocular, and an aplanatic condenser." Although the microscopic magnification was about 970x, the projection on to the screen gave larger pictures.

To reduce the disturbing influence of Brownian movement to a minimum, Campbell diluted his samples of milk with aqueous glycerol. One c.c. of milk (well mixed) was added to 9 c.c. of water, and 1 c.c. of this diluted milk was added to 9 c.c. of water and glycerol (1 : 1). The dilution was thus 1 : 100. One or two drops of the diluted milk were examined, using a hæmacytometer, covering the chamber (100 μ deep) with a cover-glass. The fat globules in ten square fields on the euscope were measured on each slide, duplication of the fields being avoided by moving the slide about. All small globules were observed as, during measurements, the microscope was focused up and down. Recording was done by an assistant to whom the sizes of the globules were called. By this technique measurements could be made on three slides from one sample in approximately thirty to forty minutes.

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[1] For summary of methods see Odén, *Soil Sci.*, **19**, 1—32 (1925); Correns, *Centr. Mineral. Geol.*, **1934 A**, 321—331; Weigel, U.S. Bur. Mines, *Tech. Paper*, **296** (1924); Gessner, " Die Schlämmanalyse " (Leipzig, 1931); Chamot and Mason, " Handbook of Chemical Microscopy " (London, 1938), pp. 408—430, section on Particle Size Determination; Wadell, *Physics*, **5**, 281 (1934); Knapp, *Ind. Eng. Chem., Anal. Edn.*, **6**, 66 (1934); Rossi, *IX Congr. intern. quim. pura aplicada*, **2**, 399 (1934).

[2] *Kolloid-Z.*, **9**, 259 (1911).

[3] *Ibid.*, **26**, 121 (1920).

[4] Vermont Agr. Expt. Sta., *Bull.*, **341**, 24 (1932).

Miss Beckett[1] has also carefully investigated the size and distribution of the fat globules in milk and cream. The milk was diluted with water to 1 : 20 and a drop transferred to a Thoma-Zeiss blood-cell of depth = 0·1 mm. A small vertical photomicrographic camera using quarter-plates was used with a Zeiss microscope of tube length of 160 mm., a 4 mm. apochromatic objective and a No. 6 compensating ocular; with camera extension of 25 cm. the magnification of 243 was secured. Good contrast in the photographs between the globules and the background was obtained by interposing a filter screen of ammoniacal copper sulphate solution, allowing light waves shorter than 0·48 μ to be transmitted. Exposures of 0·5 second were made, a carbon electric arc being the illuminant.

Counting was done over a definite area on each print, this area being marked out in squares of approximately 2 cm. side. To measure the size of the globules the Fresnel-Joly micrometer method was employed. The basis of this method is that the diameter of a circle touching two converging lines is proportional to the distances of its points of contact from the intersection of the lines. " The actual gauge used was a transparency, 5 cm. long, made from a drawing 30 cm. long, on Bristol board, and reduced to give readings in microns. The converging lines were spaced off by cross-lines at intervals corresponding to the points of contact of the images of globules, 1·5 μ, 2·5 μ, etc.; all images touching the converging lines in the interval 4·5 to 5·5 were classed as 5 μ and so on." Sufficient accuracy is attained as a large number of globules is counted, and three photographs taken (each from a separate drop) of each sample. The graphs of the results were plotted with the globule diameters (μ) as abscissæ and the percentage volume of fat (in μ^3) contained in each size class as ordinates.

Direct measurements of the globule sizes in emulsions have been described by Sibree,[2] using paraffin-in-aqueous sodium oleate systems, wherein the two phases were of equal density (thus excluding sedimentation methods of analysis).

A small portion of the emulsion was added to a warm 10 per cent.

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[1] *Econ. Proc. Roy. Dublin Soc.*, **11**, 303 (1927). Cf. Hixson and Fain, *Ind. Eng. Chem.* **24**, 1338 (1932).

[2] *Trans. Faraday Soc.*, **27**, 161 (1931).

aqueous solution of gelatin, and the whole diluted with 1 per cent. aqueous solution of sodium oleate, reducing the gelatin concentration to 5 per cent. Brownian movement was avoided by allowing a drop of the diluted emulsion to gel in a microscope slide under a cover-glass. Photomicrographs were then taken at appropriate magnifications on either dry plates or bromide paper. A series of concentric circles was drawn on transparent material which was then superimposed on the photograph. Assuming two adjacent circles of diameters $n\mu$ and $n'\mu$ respectively, then globules falling in the space between them were reckoned as possessing a diameter of $\frac{n + n'}{2}\mu$. Each globule was marked after being measured. In this way the total number of globules of diameter $\frac{n + n'}{2}\mu$ was observed, and so on for other sizes.

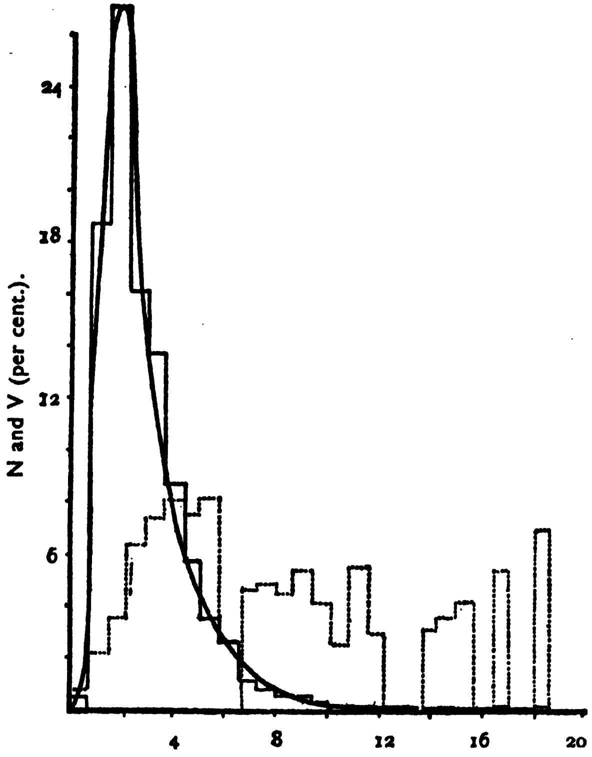

FIG. 99. Size-frequency analysis of an emulsion of viscous paraffin oil in 1 per cent. aqueous sodium oleate solution, passed through a Hurrell colloid mill (Sibree).

Both N, the percentage number of globules of each size, and V, the percentage volume of globules of each size, were calculated. Sibree plotted his results with $n\mu$ and $n'\mu$ as abscissæ and on $n'\mu$-$n\mu$ as base he drew a rectangle, the area of which represents the percentage number of globules, N, lying between these limits. In this way a series of rectangles is obtained, the total area of which on the correct scale is 100. Through the upper portion of the rectangles a graph is drawn, smoothed so that the total area bounded by the graph and the co-ordinates is 100. (By plotting V in the same manner other characteristics of the emulsion are made evident; see dotted rectangles, Fig. 99.)

Fig. 99 reproduced from Sibree's paper relates to an emulsion of viscous paraffin in 1 per cent. sodium oleate solution, using a Hurrell colloid mill to secure fine subdivision of the oil.

In 1924, Kraemer and Stamm[1] described a new method for the determination of the distribution of size of globules in emulsions. The authors examined the gravity separation (*i.e.*, cream rising) of the emulsions. The rate of change in the apparent density of the upper portion of the emulsion into which the disperse phase is rising can be interpreted to give the rate of creaming. A time-accumulation curve is thus obtained from which a size-distribution curve is derived.[2]

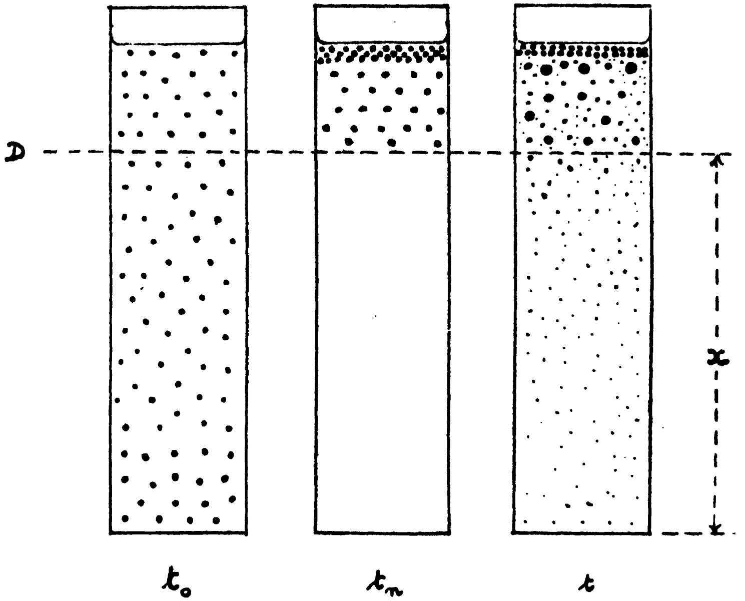

FIG. 100. Creaming of emulsions.

The apparatus used is a modification of that due to Wiegner[3] and extended by Ostwald and von Hahn.[4] A vertical tube (containing emulsion) is fitted with a capillary side-arm, which contains the pure dispersion medium. The gradual creaming of the emulsion leads to a decrease in the average density of the liquid above the plane A, accompanied by a compensating decrease in the height of the liquid in the capillary tube. It is clear that the rate of change of the meniscus in the capillary tube is a measure of the rate of accumulation of the disperse phase into the space above the plane A.

The mathematical aspect of sedimentation analysis has been dealt with by Odén,[1] Svedberg[2] and others.[3] Following Odén,[4] consider an emulsion with complete disintegration and uniform distribution of globules at the time of commencing the experiment t_0. Each globule is considered to rise independently. See Fig. 100. If all the globules had the same radius, they would rise with the same velocity and the concentration of the globules in a certain layer D would be constant up to a certain time t_n, since all disappearing globules are replaced by others coming from the layers below. Suddenly the velocity would drop to zero at a time t_n when the globules of a velocity x/t_n, which at the beginning were in the bottom layer, had passed the level D.

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[1] *J. Am. Chem. Soc.*, **46**, 2709 (1924).

[2] Svedberg, *ibid.*, **45**, 943 (1923).

[3] *Landw. Vers. Sta.*, **91**, 41 (1919); *J. Soc. Chem. Ind.*, **46**, 21 T. (1927).

[4] *Kolloid-Z.*, **30**, 62 (1922); cf. Kelly, *Colloid Symposium Monograph*, **2**, 29 (1925).

If, however, the globules are of various sizes and therefore rise with different velocities, certain groups in time disappear completely from a certain layer and the concentration there decreases continuously while the creaming proceeds.

Now consider a layer at a distance x from the bottom and at the time t from the commencement of creaming. Of all the globules of various size some groups have *completely* passed above this level and entered the cream space, viz., those whose velocity is greater than x/t (call these S), while from the other groups with velocities less than x/t there has been a constant flow of globules during the whole time t, proportional to the time and concentration.

Thus, during the creaming of an emulsion, the total quantity of cream P in a determined cream space after a time, t, can be considered as made up of two parts. One part, S, corresponds to all the groups of globules that have creamed completely (their radii being such as to permit this). The other part contains portions of those groups of globules whose radii are smaller and so require further time for creaming; each of these groups rises at a constant rate, and the rate for all groups together is $d\mathrm{P}/dt$.

After a time t, the relation holds

$$\mathrm{P} = \mathrm{S} + t\frac{dP}{dt}.$$

whence

$$\frac{d\mathrm{P}}{dt} = \frac{d\mathrm{S}}{dt} + t\frac{d^2\mathrm{P}}{dt^2} + \frac{d\mathrm{P}}{dt}.$$

or

$$\frac{d\mathrm{S}}{dt} = -t\frac{d^2\mathrm{P}}{dt^2}.$$

It is required to express S in terms of radius (r).

$$\frac{d\mathrm{S}}{dr} = \frac{\frac{d\mathrm{S}}{dt}}{\frac{dr}{dt}}.$$

From Stokes' equation,

$$r^2 = \frac{c^2}{t}.$$

$$\frac{dr}{dt} = \frac{r}{2t},$$

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[1] Alexander's "Colloid Chemistry," Vol. 1 (New York, 1926), p. 861.

[2] "Colloid Chemistry" (New York, 1924), p. 136.

[3] Cf. *J. Opt. Soc. Am.*, 11, 393 (1925); Kammermeyer and Binder, *Ind. Eng. Chem., Anal. Edn.*, 13, 335 (1941).

[4] *Soil Sci.*, 19, 12 (1925).

therefore
$$\frac{dS}{dr} = -\frac{2t^2}{r}.\frac{d^2P}{dt^2}.$$

In practice, the relation between P and t is measured, and a so-called sedimentation curve plotted. See Fig. 101 (Svedberg [1]).

At the point on the graph corresponding to time t, draw a tangent to cut the ordinate at w. Then,

$$w = P - t\frac{dP}{dt}.$$

whence
$$\frac{dw}{dt} = -t\frac{d^2P}{dt^2},$$
$$\frac{dw}{dt} = \frac{dS}{dt}.$$

Hence the dS values may be determined by drawing tangents from the graph (at points corresponding to equal time intervals) to the ordinate.

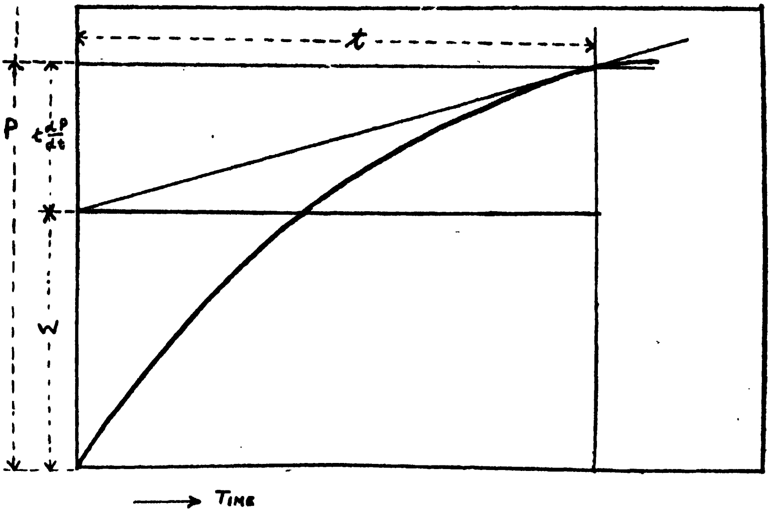

Fig. 101. Sedimentation curve.

dS is thus the distance between the ordinary intercepts of two successive tangents. The corresponding dr values are calculated on the basis of Stokes' equation, since the time, distance traversed, viscosity of the medium, and densities are known.

The apparatus of Kraemer and Stamm was mounted on a wooden frame and clamped securely to a vertical rod in a thermostat. If:

A = cross-sectional area of the plane A.
s = cross-sectional area of the capillary.
d_m = density of pure dispersion medium.
d_p = density of disperse phase.
θ = the angle of the capillary.

it can be shown that P, the weight of disperse phase passing the plane A during creaming, is equal to:

$$\frac{d_p \,.\, d_m}{d_m - d_p}\left(A \sin\theta + s\right)\left(a - b\right),$$

"Colloid Chemistry" (New York, 1924), p. 145.

where a and b are the initial and subsequent readings of the meniscus in the capillary. Thus an accumulation curve may be constructed to show the relationship between P and time.

Fig. 102 reproduced from Kraemer and Stamm's paper, is the accumulation curve of an emulsion of 10 per cent. benzene emulsified in water containing 0·0005 N potassium palmitate. The corresponding distribution curve is obtained by plotting radius of the globules (in μ) as abscissæ against $\frac{dS}{dr}$ as ordinates. Obviously, the area under any portion of this curve corresponds to the actual weight of benzene dispersed as globules whose radii vary between the values represented by the bounding abscissæ.

Where emulsions are employed in which the disperse phase sinks, *e.g.*, water-in-benzene, the capillary tube meets the vertical tube near the bottom. An automatic method of recording the meniscus change is described by Lambert and Wightman.[1]

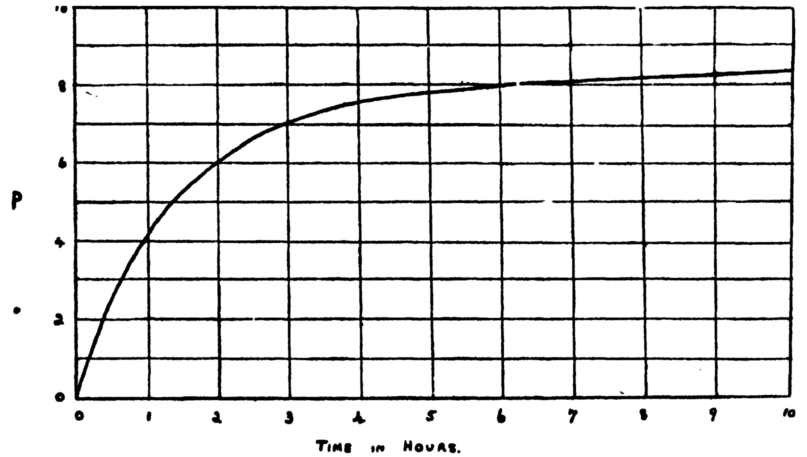

FIG. 102. Size-frequency analysis of emulsions : a typical accumulation curve (Kraemer and Stamm).

Another method for the determination of the distribution of size of globules in emulsions has been used by Stamm and Svedberg,[2] and by Stamm.[3] The concentration of the emulsion after periods of creaming was determined photometrically by the intensity of the scattered light at right angles to the source. The emulsion was contained in a narrow cell with a dark opaque background and was illuminated from the sides. The intensity of the light scattered to the front was recorded photographically and the densities on the photographic plate determined with a photometer. The method is particularly suited for emulsions of less than 5 per cent. disperse phase and for slow-creaming emulsions.

Sumner[4] has considerably modified and improved the methods of Kraemer and Stamm and Lambert and Wightman by introducing a

[1] *J. Opt. Soc. Am.*, **11**, 393 (1925).

[2] *J. Am. Chem. Soc.*, **47**, 1582 (1925).

[3] *Colloid Symposium Monograph*, **3**, 251 (1925).

[4] *J. Phys. Chem.*, **37**, 279 (1933); *J. Sci. Instruments*, **7**, 398 (1930).

new type of sedimentation tube and a new method of operating a discontinuous automatic recording camera. Benzene is employed as the index liquid and a simple correction is made for the effect of viscosity in the index tube.

All the above methods for determining size-frequency analyses are admittedly tedious and for rapid routine work in the technical control of emulsions a simpler analysis is desirable. Smith and Grinling [1] have developed such a scheme for their control of pharmaceutical emulsions. Pointing out that in an emulsion much of the oil may be poorly dispersed without producing more than a few large globules and that a very small amount of the total oil may be finely dispersed, so producing a great number of minute globules (having an influence on the average diameter of globules inordinately proportional to their significance), they overcome such difficulty by taking a mean of the *volumes* of the globules. " In this way a few large globules, which have little effect on the mean diameter, considerably affect the mean volume, while large numbers of tiny globules have no more than their due effect. The mean volume of a globule in c.c. or its reciprocal, the number of globules into which 1 c.c. of oil is subdivided, is in fact the most satisfactory single criterion of the efficiency of emulsification."

Smith and Grinling count the globules directly using a Thoma hæmocytometer, the central portion, 0·1 mm. deep, ruled into squares 0·0025 mm.^{2} in area. A weighted quantity of emulsion is suitably diluted in 25 per cent. gum acacia mucilage, 1 grm. of emulsion + 25 c.c. mucilage, and then further diluted so that when a few drops are placed on the central portion of the hæmocytometer, one square will contain 10 to 20 globules. Examination is made with a $\frac{1}{6}$-inch objective and No. 4 eye-piece.

At least ten squares are counted and the minute globules searched for, the full depth of the field being examined by varying the focus. They express the degree of emulsification H as the number of millions of globules furnished by 1 mm.^{3} of the oil. Thus, H, which is independent of the concentration of emulsion, is the product of the number of globules per square (n), $4{,}000 \times 10^{-6}$, the volume to which 1 grm. of emulsion is diluted and the weight of emulsion containing 1 c.c. of oil.

For example, for an emulsion containing 30 per cent. oil, when 1 grm. is diluted to 1,000 c.c.

$$H = n \times 4{,}000 \times 10^{-6} \times 1{,}000 \times 3{\cdot}7$$

or

$$H = 13{\cdot}1\, n.$$

Assuming H is fixed at 200, then $n = 15$. " In other words, it would only be necessary to determine whether a batch of emulsion gives 15 or more globules per square under the conditions specified, to know whether it may be passed as satisfactory."

It is pointed out that the value of H not only indicates the efficiency of emulsification, but, for an emulsion of any given composition, indicates the creaming possibility on storage.

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[1] *Quart. J. Pharm. Pharmacol.*, **3**, 354 (1930).

Smith and Grinling further develop their method by determining D, the *root mean cube diameter*, a quantity in general larger than the arithmetical mean. Thus, $D = 10\sqrt[3]{\frac{6}{\pi H}}\,\mu$. This value is equivalent to the figure obtained by cubing the measured diameter of numerous globules and determining the cube root of their average. D indicates the diameter the globules would possess, assuming they were all uniform in size and equal in number to the globules in the emulsion examined. The data in Table 54 are reproduced from the authors' paper.

TABLE 54

EFFECT OF HOMOGENISATION OF SIZE-FREQUENCY ANALYSIS

	50 per cent. Cod-Liver Oil Emulsion.		
	Stabilised by 1 per cent. Soap.		Stabilised by Gum.
	Before Homogenisation.	After Homogenisation.	
Arithmetical Mean Diameter	$4{\cdot}5\mu$	$2{\cdot}3\mu$	$5{\cdot}3\mu$
D Measured	—	$3{\cdot}0\mu$	$10{\cdot}0\mu$
D Counted	$9{\cdot}0\mu$	$2{\cdot}5\mu$	$8{\cdot}4\mu$
Globules per c.c.			
Measured	—	75×10^9	2×10^9
Counted	$2{\cdot}6 \times 10^9$	120×10^9	$3{\cdot}2 \times 10^9$

A new treatment of the subject is by Miss Berkman,[1] who has developed a statistical method, using a new type Leitz microprojection equipment with a special collinator of great light-transmitting power. Her emulsions of paraffins in Na oleate solutions (see p. 181) were diluted with 300 volumes of distilled water for observation. Projection of the microscope slide was made on a screen of millimeter graph paper at such distance that each millimeter of the graph paper corresponded to 1 micron.

Size frequencies were obtained by calculating the number of globules of various sizes. The method of obtaining the distribution curves was statistical, using the law of great numbers to increase the probability. Each distribution curve involved the calculation and measuring of an average of 1,500 to 2,000 globules. From the calculated number of globules of each size and the total number of globules calculated, the percentage of globules of each size was determined.

For the investigation of the kinetics of changes as reflected in the size-frequency analyses, small rates of changes of the physical quantity were studied by mathematical analysis. "The distribution of sizes and the corresponding percentage of droplets obtained experimentally were plotted for each emulsion directly in a co-ordinate system as integral curves, and from these integral curves, derivative curves were constructed.

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[1] *J. Phys. Chem.*, **39**, 527 (1935).

For the evaluation of the derivative $y' - \frac{dy}{dx}$, when the function is known analytically, a different calculus or a graphical method must be used. Geometrically, the procedure consists in using the principle that the ordinate of the derivative curve at any point $P'(x, y)'$ is equal to the slope of the integral curve at any point, that is, of the tangent at the corresponding point of the integral curve.

"The practical construction of the derivative curve is as follows (Fig. 103): A point S $(-2, 0)$ is chosen at a convenient distance to the left of the axis y and a line parallel to the tangent drawn for each point of the integral curve. This parallel cuts the ordinate axis at the point U. Since SU forms with the axis $+x$ the same angle α as the tangent t, then $OU = tg\alpha = y'$ and the point U projected horizontally on the ordinate from the point P cuts it at P′, which is the point of the derivative curve

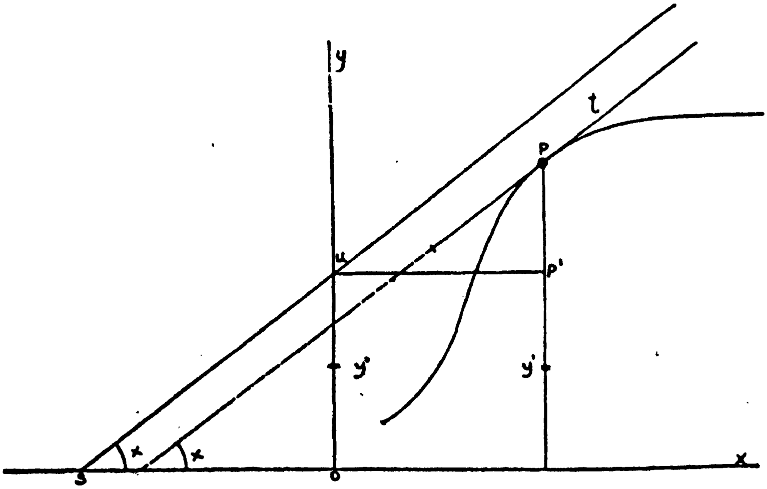

FIG. 103. Construction of a derivative curve (Berkman).

corresponding to the point P of the integral curve. Since $Y' = 1/afy \,.\, dx$, then $dy/dx = 1/aY$. The slope of the integral curve at any point is proportional to the ordinate of the derivative curve at the corresponding point."

An exhaustive examination of the basis of size-frequency distributions has been made by Cooper,[1] who worked with 60 O/W emulsions (refined, paraffin oil in aqueous potassium oleate, passed through a Hurrell colloid mill).

Cooper's paper deserves close study by the experimenter in this field, as it analyses thoroughly the mathematical principles involved in the size-frequency distributiion, and gives reasons for the choice of working bases. He concludes that the best figure to define an emulsion is the specific surface, *i.e.*, the total surface area per c.c. of dispersed oil. It is a direct measure of the work done in creating the emulsion.

It is pointed out that none of the usual size-frequency distribution equations will fit the observed distributions, which appear to be built up from two separate distributions. One, which represents the main bulk of the dispersed phase, can be represented by Rossi's theoretical equation (based only on considerations of probability).[1] The other appears to be a J-shaped distribution of an exponential type, and probably corresponds to very small subsidiary drops formed between each pair of the larger drops in the production of the emulsion.

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[1] Ph.D. thesis, London, 1936. Summarised in *J. Soc. Chem. Ind.*, **56**, 447 T. (1937).

Other papers dealing with this subject are by Kraemer [2] who presents a detailed mathematical study of the determination of average particle sizes for polydispersed systems, Richardson,[3] dealing with the physical properties of disperse systems, Hvidberg [4] who describes a reproducible method for the accurate microphotographic representation of dispersions, Weeks [5] on the effect of hydrogen ion concentration on the measurement of the mean particle size of emulsions, Davey [6] describing a surface-spreading technique and the use of the Langmuir balance for determining the average diameter of the emulsion globules. The particle size determination of colloidal systems by the supercentrifuge has been reported by Hauser and Schachman.[7] Figurovskii has described photoelectric methods [8] and sedimentation analysis.[9]

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[1] *Gazz. chim. ital.*, **63**, 190 (1933).
[2] *J. Franklin Inst.*, **231**, 1 (1941).
[3] *Science Progress*, **31**, 462 (1937).
[4] *Kolloid-Z.*, **72**, 274 (1935).
[5] *Phys. Rev.*, **35**, 668 (1930).
[6] *J. Phys. Chem.*, **35**, 115 (1931).
[7] *Ibid.*, **44**, 584 (1940).
[8] *Zavodskaya Lab.*, **7**, 1076 (1938).
[9] *Ibid.*, **8**, 68 (1939).

APPENDIX I

(Unchanged from the 3rd Edition)

THE SEPARATION OF TECHNICAL EMULSIONS PARTICULARLY CRUDE OIL-FIELD EMULSIONS

Use of Antagonistic Emulsifying Agents. Whilst many of the proposed chemical agents for de-emulsification are of a mixed chemical nature, classification may be made as follows :—

Naphthenic Compounds. The pioneer patent seems to be that of Berkhahn,[1] claiming the addition to the crude oil of kerosene-naphthenic acids. Barnickel [2] uses halogen or nitro-derivatives of resin, whilst Behm [3] mentions resin-alkali compounds. Kaplan [4] discloses a treating agent comprising a combined sulphonated rosin oil such as a rosin oil sulphonated in admixture with castor oil. De Groote and Wirtel hold several patents, such as a (*a*) [5] sulphoabietic acid or its Na salt; (*b*) [6] anhydrous Na salt of a naphthenic acid, produced from naphthenic acids of a molecular weight of from 200 to 575, a mean molecular weight of about 225, and a distillation range of from 230° to 310° C., mixed with a relatively small amount of an un-neutralised naphthenic acid of the same kind; (*c*) [7] a mixture comprising not over 40 per cent. of water, material produced by partial neutralisation with NH_4OH of naphthenic acids already described, and about an equal amount of a water-soluble ammonium salt of a butylated naphthalene sulphonic acid; (*d*) [8] De Groote mentions an oil- and water-soluble demulsifier containing not more than 40 per cent. of water together with a dialkyl polysulphonate ammonium salt produced from Blau gas tar by reaction with H_2SO_4 at 40° C., and an equal amount of a naphthenic acid or naphthenate as already described; (*e*) [9] similar naphthenic acids or their salts together with an ammonium compound of a petroleum sulphonic acid substantially free from polymers and non-sulpho type hydrocarbons and derived from Gulf Coast naphthene crude oil by multiple acid treatment of the kind in which the first acid draw-off is discarded; (*f*) De Groote and Wirtel [10] claim the use of an agent derived from the chemical reaction of an abietine-nucleus hydrocarbon such as abietine, an aldehyde such as CH_2O and a sulphonating agent.

Sulphonated Compounds. An extraordinary range of sulphonated compounds exhibits the importance of the addition of chemical demulsifying agents to crude oils. Several main groups of such compounds may be delimited.

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[1] Russian 26,671 (1913). The subject is dealt with by Pyhälä, *Erdöl u. Teer*, 6, 478 (1930); Geritz, *Allgem. osterr. Chem. Tech. Ztg.*, 48, 27 (1930); 11e *Congres international de forage*, 1929, 1—7.

[2] U.S. 1,555,818 (1925).

[3] U.S. 1,541,242—3 (1925).

[4] U.S. 1,902,129 (1933). Ayres mentions Na resinate and free resin, U.S. 1,454,616—7 (1923).

[5] U.S. 1,910,680 (1933).

[6] U.S. 1,940,391 (1933).

[7] U.S. 1,940,392 (1933).

[8] U.S. 1,940,395 (1933).

[9] U.S. 1,940,396 (1933).

[10] U.S. 1,961,963 (1934).

Walker[1] advises the ammonium salt of sulpho-stearic acid, whilst Kaplan[2] used a composition of sulphonated linseed oil and raw linseed oil. Herbsman[3] subjects the emulsion to the action of a treating agent which is capable of hardening water and includes a mixture of a sulphonated fatty glyceride, an alkaline-earth salt such as $MgCl_2$ and a suitable solvent such as an alcohol or phenol. According to Hinrichs,[4] ricinoleic or lactic acid is heated to remove combined water and the product is used alone or after treatment with an alkylsulphonic acid. The sulphonation of a mixture of equal parts of rosin oil and castor oil is claimed by Kaplan.[5] De Groote and Monson[6] mention the sulphuric ester of cetyl alcohol (or its ammonium salt), and the Na salt of a sulphonic acid derived from lauryl alcohol.[7] Wayne[8] describes a complex condensation product prepared from a sulphonated aromatic amine, such as sulphonated aniline and an alcohol or aldehyde of the aliphatic series. Walker[9] claims an alkaline salt of an alkylated polycyclic sulphonic acid, whilst an acetylated derivative of a hydroxylated fatty acid is also featured,[10] *e.g.*, acetylsulphoricinoleic acid. Keiser's[11] treating agent contains sulpho-oleic acid and approximately 80 per cent. of oleic acid and other compounds, *e.g.*, stearolactone, hydroxystearic acid, etc.

De Groote and Adams claim a variety of agents: (*a*)[12] a mixture of 30 per cent. of reagent of the Twitchell type or other hydroxy monocyclic sulpho-aromatic detergent, about 30 per cent. of oleic compounds or of other detergent-forming material uncombined with aromatics and about 20 per cent. of non-hydroxy tar acid oil aromatics, with water; (*b*)[13] a mixture of condensation product (such as one containing NH_4 salts of sulphonated naphthol combined with modified oleic acid) containing a sulphonated hydroxy polycyclic aromatic combined with a soap-forming material; (*c*)[14] condensation product produced by subjecting a hydroxylated soap-forming acid such as hydroxystearic acid and a sulphonate of an aromatic hydrocarbon, *e.g.*, phenol-monosulphonate, to the action of H_2SO_4 or other dehydrating agent; (*d*)[15] sulphonate a mass composed of oleic acid or other soap-forming organic acid and an aromatic compound such as phenol in which the proportion of aromatic molecule to soap-forming molecule exceeds 1 : 1; (*e*)[16] subject olein or other soap-forming acid in which the COOH group is blocked and non-reactive to the action of an aromatic compound such as phenol or cresol in the presence of a sulphonating agent; (*f*)[17] reaction is effected between an aromatic sulphonic acid such as naphthalene-sulphonic acid and an organic soap-forming group such as ricinoleic acid which is susceptible to reaction with

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[1] U.S. 1,829,205 (1931).

[2] U.S. 1,897,021 (1933).

[3] U.S. 1,959,824 (1934).

[4] U.S. 1,901,163 (1933).

[5] U.S. 1,902,129 (1933).

[6] U.S. 1,938,322 (1933).

[7] U.S. 1,938,323 (1933).

[8] U.S. 1,937,259 (1933).

[9] U.S. 1,944,021 (1934).

[10] De Groote *et al.*, U.S. 1,812,393 (1931).

[11] U.S. 1,659,998 (1928).

[12] U.S. 1,656,622 (1928).

[13] U.S. 1,656,623 (1928).

[14] U.S. 1,659,993 (1928).

[15] U.S. 1,659,994 (1928).

[16] U.S. 1,659,995 (1928).

[17] U.S. 1,659,996 (1928).

H_2SO_4; (*g*)[1] reaction is effected between a $C_{10}H_8$-castor oil product or other aromatic sulpho-soap-forming acid and an oleic acid and hydroxystearic acid product or other organic soap-forming group which is susceptible to reaction with H_2SO_4.

De Groote and Wirtel claim: (*a*)[2] ammonium naphthenates with water-soluble ammonium salts of butylated naphthalene sulphonic acid, or (*b*)[3] the latter salts with a product derived by the partial saponification of oleic acid with NH_4OH diluted with kerosene; (*c*)[4] a similar reagent utilises an oil-soluble, water-insoluble petroleum sulphonic acid instead of oleic acid; (*d*)[5] a mixture of a product obtained by hydrolysis of sulphonated castor oil together with a water-soluble salt of a butylated naphthalene sulphonic acid; (*e*)[6] a mixture of an oil-soluble, water-insoluble petroleum Na sulphonate, a modified fatty acid product partially saponified with NH_4OH, dilute alcohol and a hydrophobe solvent such as kerosene, together with neutral compatible salts of inorganic acids in specified proportions.

According to De Groote and Keiser[7] there may be used sulphoaryl esters of higher aliphatic or naphthenic acids, which may be modified by addition at a double linking or acylation of OH. Thus, Na sulphobenzyl ricinoleate (490 parts) is heated with *o*—$C_6H_4(CO)_2O$ (148 parts) in xylene at 120°—130° C.

Other patents by De Groote are: (1)[8] the demulsifying agent is of the general formula $RTZSO_3R'$, such as a reaction product of naphthalene, cyclohexanol and H_2SO_4, washed and treated with NH_3. Here, R = an aromatic residue, T = a H atom thereof or a substituent atom or a hydroxyl group, Z = the H-ion equivalent of the sulphonic acid residue and R′ = a reactive hydroaromatic residue; (2)[9] the mixture comprises (*a*) a water-soluble sulpho material like the triethanolamine salt of dioxalyl-triricinolein which does not precipitate when free from other materials in the presence of an alkaline earth salt and (*b*) a water-soluble demulsifying agent such as Na salts of oleic acid H sulphate which forms a precipitate with alkaline earth salts. The constituents *a* and *b* are employed in the ratio corresponding to their average molecular weights, and the combined mixture is capable of being precipitated in its entirety by alkaline earth salts; (3)[10] the agent contains a sulpho-aliphatic ester of a fatty acid of the type $R''.COO(T.SO_3.Z)$, in which R″ = a fatty acid radical, T = an aliphatic residue, and Z = the acidic H atom of the sulphonic acid or its equivalent. $(T.SO_3.Z)$ replaces the carboxylic H atom, such as a soluble NH_4 salt of the hydroxyethane sulphonic ester of phthalylricinoleic acid; (4)[11] the agent is produced by reacting oleic acid with sulphuric acid monohydrate and then with gaseous SO_3, followed by a washing process and neutralisation with concentrated ammonia; (5)[12] wood sulphite liquor is used in the demulsifying agent, or (6)[13] a water-soluble derivative of lignin, *e.g.*, Mg lignosulphonate; (7) [1] wood sulphite liquor is used with an organic saponaceous material like the NH_3 product of sulphonated castor oil; or (8) [2] a propylated naphthalene sulphonic acid; (9) [3] the reagent comprises a propylated and amylated derivative of an aromatic sulphonic compound, or (10) [4] similar compounds containing a bicyclic aromatic nucleus; (11) [5] the ammonium salt of amylnaphthalenesulphonic acid or analogous compound, which forms insoluble Ca or Mg salts; (12)[6] sulphonate the unseparated constituents of anthracene oil and mix with oleic acid; wash and neutralise with ammonia.

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[1] U.S. 1,659,997 (1928).
[2] U.S. 1,940,392 (1933).
[3] U.S. 1,940,393 (1933).
[4] U.S. 1,940,394 (1933).
[5] U.S. 1,940,397 (1933).
[6] U.S. 1,940,398 (1933).
[7] U.S. 1,954,585 (1934).
[8] U.S. 1,988,832 (1935).
[9] U.S. 1,988,834 (1935).
[10] U.S. 1,988,835 (1935).
[11] U.S. 1,926,715 (1933).
[12] U.S. 1,766,057 (1930).
[13] U.S. 1,766,058 (1930).

Wayne [7] breaks the emulsions by addition of a water-soluble (resinous) condensation product from an aldol and an amide of $H_2CO_3.CH_2O$ and PhOMe (sulphonated), a polyhydric alcohol, an unsaturated fatty acid, and an aromatic dibasic acid or anhydride (sulphonated), or from a $(.CH_2Ph)_2$ compound and an aromatic sulphonic acid. He also [8] treats with a highly colloidal condensation product of a dialkylnaphthalenedisulphonic acid and an aromatic amine, such as aniline, toluidine or diphenylamine, having its NH_2 or NH group directly attached to the aromatic nucleus. Further, he specifies [9] the reaction product of trimethylamine and sulphonated castor oil.

According to Claytor [10] the agent comprises a water-soluble product derived from the reaction between a non-hydroxy aromatic hydrocarbon, such as naphthalene, benzene, toluene, or xylene, a saturated series aldehyde compound (such as CH_2O or methylal) and H_2SO_4, intimately associated with a sulphonated fatty material. Canfield's patent [11] mentions a liquid mixture of an isopropylnaphthalenesulphonic compound, water, cresylic acid and a low freezing halogen derivative of an aromatic hydrocarbon such as PhCl. Roberts [12] claims a water-soluble salt of a mixture comprising a fatty acid, an aromatic sulphonic acid (*e.g.*, phenolsulphonic acid), and a sulpho-aromatic fatty acid dissolved in or mixed with an alcohol, unsaponified fatty material such as "red oil" and a non-sulphonated aromatic substance like phenol.

Related compounds figure in patents by De Groote and his associates: (1) [13] a sulphonic product derived from the condensation of an aromatic material like naphthalene, an aldehyde like CH_2O and an organic detergent like sulphonated castor oil; (2) [14] from the condensation of an aromatic material such as naphthalene and an aldehyde such as CH_2O, there is derived a sulphonic material; (3) [15] the aromatic sulphonic product is derived by condensation of an aromatic material such as naphthalenesulphonic acid and a ketone such as di-Pr ketone, or (4) [16] an aliphatic polyhydric alcohol, such as ethylene glycol, containing less than 12 C. atoms; (5) an amylated aromatic compound, [17] such as an ammonium amylated aromatic sulphonate capable of producing an insoluble precipitate with a soluble alkaline earth salt; (6)[1] a substituted aromatic detergent-forming sulphonic compound of the type $XFRSO_3Z$, where X = a polycyclic aromatic nucleus, F = a detergent-forming organic residue, R = a residue of an alcohol containing less than 12 C. atoms and substituted in the aromatic ring, and Z = a H-ion equivalent; (7)[2] an acetylated derivative of a hydroxylated fatty acid, such as acetylsulphoricinoleic acid; (8)[3] a chlorinated sulpho fatty compound in which the Cl is directly attached to the aliphatic acid radical, and derived from castor oil in the form of an NH_4 salt; (9)[4] an oil-soluble sulphonated derivative of hydrogenated castor oil; (10)[5] the Na salt of a sulphonic acid derived from tetradecyl alcohol.

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[1] U.S. 1,766,060 (1930).
[2] U.S. 1,780,343 (1930).
[3] U.S. 1,897,574 (1933).
[4] U.S. 1,897,575 (1933).
[5] U.S. 1,780,344 (1930).
[6] U.S. 1,975,839 (1934).
[7] U.S. 1,912,330 (1933).
[8] U.S. 1,860,562 (1932).
[9] U.S. 1,860,563 (1932).
[10] U.S. 1,773,517 (1930).
[11] U.S. 1,858,186 (1932).
[12] U.S. 1,659,999 (1928).
[13] U.S. 1,766,061 (1930).
[14] U.S. 1,766,062 (1930).
[15] U.S. 1,766,066 (1930).
[16] U.S. 1,766,067 (1930).
[17] U.S. 1,780,344 (1930).

Since sulphonated petroleum compounds, as, for instance, obtained from petroleum refining, are notably good agents for promoting O/W emulsions (see p. 118), it is not surprising to find many patents claiming these compounds, in quite simple form.[6] They are used, too, in more complex unions. Myers[7] mixes the water-soluble mineral oil sulphonates with modified fatty acids, such as sulpho fatty aromatic acid products, whilst Walker[8] suggests a mixture of sulphonated crude turpentine, and the NH_4 salt of a sulpho fatty acid, De Groote[9] specifies cresylic acid and a petroleum sulphonic compound, or[10] the acids from petroleum refining chemically combined with fatty material, *e.g.*, castor oil. With Monson he claims (*a*)[11] a petroleum sulphonic product which may be derived from the condensation of a petroleum sulphonic material and an alcohol (such as PrOH) containing less than 12 C. atoms, or (*b*)[12] an aldehyde such as CH_2O, instead of the alcohol, or (*c*)[13] a ketone. A polyhydric alcohol of less than 12 C. atoms, such as ethylene glycol, may be used.[14] With Wirtel[15] he specifies a mixture of not more than 40 per cent. of water, together with a water-soluble NH_4 salt of a butylated naphthalene sulphonic acid and a product derived from petroleum sulphonates.

The use of tarry materials is referred to in several specifications. Lerch[16] uses the reaction product of sulphonated cotton-seed oil with a chlorinated tarry material formed by chlorinating tarry material of the polyolefin, cyclopentene and cyclohexene series, such as a Blau gas tar. Curtin[17] advises the addition to the crude oil of 0·5 to 4 per cent. by volume of the oil content of low temperature tar, followed by heating to at least 70° C. for several minutes. De Groote[18] produces the demulsifier by the reaction of approximately molecular proportions of naphthalene and Pintsch gas tar middle distillate and comprising cyclo-olefins having not less than 7 C. atoms and not more than 17 C. atoms in the ring, with a large excess of concentrated H_2SO_4, followed by washing and neutralisation with ammonia. Kaul[1] mentions a mixture of black strap molasses, glucose or glycerin, and cresol, coal-tar creosote or wood creosote. It is interesting to note Fuchs' patent[2] where pine oil is employed to decrease the viscosity at low temperatures of emulsion breakers containing a sulphonated oil compound.

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[1] U.S. 1,780,345 (1930).

[2] U.S. 1,812,393 (1931).

[3] U.S. 1,908,130 (1933).

[4] U.S. 1,940,390 (1933).

[5] U.S. 1,943,815 (1934).

[6] Rogers, U.S. 1,299,385 (1919); Pester, U.S. 1,669,379 (1928); Standard Oil Development Co., Brit. 319,623 (1928); Moser, U.S. 1,788,684 (1931); Burgess, U.S. 1,668,941 (1928); Gray, U.S. 1,673,045 (1928); Payne and Montgomery, U.S. 1,726,309 and 1,726,310 (1929); Fischer and Reddish, U.S. 1,734,369 (1929); Coggeshall and Reilly, U.S. 1,742,648 (1930); Myers, U.S. 1,837,130 (1931); Peirce and Myers, U.S. 1,882,444 (1932).

[7] U.S. 1,834,228 (1931).

[8] U.S. 1,863,143 (1932).

[9] U.S. 1,660,004 (1928).

[10] U.S. 1,660,005 (1928).

[11] U.S. 1,766,063 (1930).

[12] U.S. 1,766,064(1930).

[13] U.S. 1,766,065 (1930).

[14] U.S. 1,766,112 (1930).

[15] U.S. 1,940,394 (1933).

[16] U.S. 1,890,789 (1932).

[17] U.S. 1,973,430 (1934).

[18] U.S. 1,985,720 (1934).

Oxidised petroleum products have been discussed as O/W emulsion promoters. Their use as demulsifiers for W/O systems is, therefore, expected. Burwell[3] uses oxidised mineral oil hydrocarbons, whilst Fuchs[4] claims a blown-oil soap formed with an alkali and to which diethylene glycol is added. Roberts[5] describes an agent which is obtained by chlorination of the crude aldehyde-containing oxidation product derived by partial oxidation of a petroleum distillate. The use of an oxidised product from hydrocarbon motor fuel produced by vapour-phase cracking of high boiling-point hydrocarbons is claimed by Hyman and Schlandt.[6]

ELECTRICAL METHODS OF DE-EMULSIFICATION

An astonishing number of patents deal with the technique or the apparatus of electrical means of de-watering crude-oil emulsions. Some of the more interesting patents are :—

(1) Seibert and Brady.[7] The oil is passed in a flowing stream between a pair of electrodes between which a potential of 250—600 volts is maintained, spaced sufficiently far apart to prevent the passage of any substantial amount of current. The electrodes may be of tubular form and concentrically placed.

(2) McKibben.[8] A continuous uninterrupted substantially uniform electric field is provided between electrodes within a conduit constituting a relatively long path to polarise the water globules tending to chain formation and the emulsion is moved through the field at such a velocity as to break up or prevent persistence of chains of polarised globules of entrapped liquid between the electrodes.

(3) McKibben.[9] The emulsion is heated sufficiently to produce vaporisation and then it is passed through an intensified electric field. The vapours are condensed and the liquids are cooled below the vaporising temperature and subsidence of the water is allowed to occur.

(4) Alden and Eddy.[10] The oil is subjected to the coalescing action of an electric field between immersed electrodes with intermittently increased and decreased intensity.

(5) Meredith.[11] The emulsion is forced by a propeller in contact with a rotating electrode between plates which guide the flow.

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[1] U.S. 1,523,220 (1925).

[2] U.S. 1,890,849 (1932).

[3] U.S. 1,993,646 (1935).

[4] U.S. 1,929,399 (1933).

[5] U.S. 1,979,347 (1934).

[6] U.S. 1,811,177 (1931).

[7] U.S. 1,290,369 (1919).

[8] U.S. 1,299,589 (1919).

[9] U.S. 1,299,590 (1919).

[10] U.S. 1,394,462 (1921).

[11] U.S. 1,452,207 (1923).

(6) Dehydrators Inc.[1] The emulsion is passed through an earthed vessel containing an electrode fed with alternating current. The potential of the current and/or the distance between the electrode and the vessel wall are such that the vessel wall lies outside the zone of charged water globules formed around the electrode.

(7) Gage.[2] The oil flows upwards between successive sets of electrodes, the spacing of these being reduced as the resistance of the emulsion increases. The P.D. between the electrodes is controlled by the amount of current flowing.

(8) Worthington.[3] The emulsion is introduced within an inner perforated rotatable electrode and passed through the perforations of this electrode into a surrounding drum which constitutes the other electrode.

(9) Eddy.[4] Before subjecting the emulsion to the action of an electric field, the dispersed globules are mechanically agglomerated (suitably by the action of excelsior or steel wool).

(10) Eddy.[5] The crude is subjected to the action of a primary electric field to divide the emulsion into a clean oil and a sludge ; the latter is washed with hot water to separate the residue emulsion, which is now mixed with a chemical demulsifier and dry oil and again subjected to the action of a secondary electric field, where the P.D. differs from that of the primary field.

(11) Morrell.[6] Finely-divided water-insoluble conducting material such as iron powder is suspended in the emulsion, an electric current is then passed and the water is subsequently sedimented.

(12) Morrell.[7] Finely-divided metal is added to the crude and this is then subjected to the action of an alternating current at 550—33,000 volts.

(13) Fisher.[8] Emulsions which are not susceptible to usual electric dehydration are mixed with Na_2CO_3 under high pressure to invert the emulsion, and this is then subjected to a high-potential electric field.

(14) Eddy.[9] The emulsion is drawn into a closed tank from which all air has been previously exhausted and is maintained under sub-atmospheric pressure and broken by electric discharges in the tank.

(15) Lawrason.[10] The emulsion is subjected to mechanical vibration both while in a pre-treatment zone and while passing between high-tension electrodes.

(16) Herbsman.[11] Treat the emulsion with a chlorinated oil, *e.g.*, chlorinated paraffin wax, and then electrically dehydrate.

(17) Roberts.[12] The emulsion is subjected to the action of an electric field of an alternating high-potential character produced by the use of a non-oscillatory alternating potential of a frequency between 60 and 10,000 cycles per second.

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[1] Ger. 526,210 (1928).
[2] U.S. 1,754,009 (1930).
[3] U.S. 1,783,595 (1930).
[4] U.S. 1,796,750 (1931).
[5] U.S. 1,826,276 (1931).
[6] U.S. 1,827,276 (1931).
[7] U.S. 1,827,714 (1931).
[8] U.S. 1,838,379 (1931).
[9] U.S. 1,847,602 (1932).
[10] U.S. 1,942,480 (1934).
[11] U.S. 1,931,112 (1933).
[12] U.S. 1,959,385 (1934).

Electrical methods have been described by Piersol,[1] Eddy,[2] Sawdon[3] and Wyant.[4]

Prominent U.S. patents on the subject are listed below :—

Averill	1,617,740 (1927)
Brey	1,570,209 (1926)
Chase	1,539,647 (1925)
Dahlstrum	1,591,286 (1926)
Eddy (H. C.)	1,544,528 (1925)
	1,466,208 (1923)
	1,442,608 (1923)
	1,838,375 (1931)
	1,838,376 (1931)
	1,847,602 (1932)
	1,779,695 (1930)
	1,838,909 (1931)
	1,838,910 (1931)
	1,838,911 (1931)
	1,838,912 (1931)
	1,838,913 (1931)
	1,838,914 (1931)
	1,838,915 (1931)
	1,838,916 (1931)
	1,838,917 (1931)
	1,963,325 (1934)
Eddy (W. O.)	1,674,242 (1928)
	1,838,918 (1931)
	1,838,919 (1931)
	1,838,920 (1931)
	1,838,374 (1931)
Egloff and Morrell	1,559,036 (1925)
Fisher	1,838,933 (1931)
	1,838,930 (1931)
	1,838,934 (1931)
	1,838,921 (1931)
	1,838,922 (1931)
	1,838,923 (1931)
Fisher (*continued*)	1,838,924 (1931)
	1,838,925 (1931)
	1,838,926 (1931)
	1,838,927 (1931)
	1,838,928 (1931)
	1,838,929 (1931)
	1,864,721 (1932)
	1,864,722 (1932)
	1,864,723 (1932)
	1,974,451 (1934)
Gassaway	1,838,822 (1931)
Girvin	1,838,937 (1931)
	1,838,938 (1931)
Harris	1,455,139 (1923)
	1,838,828 (1931)
Hanson	1,978,793 (1934)
Howes	1,891,645 (1932)
Lawrason	1,838,847 (1931)
	1,838,848 (1931)
	1,838,849 (1931)
	1,838,850 (1931)
Leonen	1,838,889 (1931)
	1,838,890 (1931)
	1,847,541 (1932)
	1,932,715 (1933)
	1,978,794 (1934)
Meredith	1,440,835 (1923)
Stevens	1,533,711 (1925)
Worthington	1,838,976 (1931)
	1,838,977 (1931)
	1,838,978 (1931)
	1,838,979 (1931)
	1,838,980 (1931)

MISCELLANEOUS METHODS

The use of solid powders to break crude-oil emulsions is claimed by Robinson,[5] who states that the emulsion is to be simultaneously and intimately contacted with a relatively large quantity of a coarsely-powdered solid and a relatively small quantity of a finely-powdered solid. Both solids used are insoluble, and are chemically inert to all the constituents of the emulsion and have adhesion tension with the dispersed liquid not substantially less than 2·5 times their adhesion tension with the continuous phase and a density materially different from that of the emulsion. The proportion of fine solid is controlled so as to produce resolution of the emulsion at a desired rate.

Lant and Koreska[6] treat the emulsion with higher fatty acid esters of cellulose or of near derivatives of cellulose, the emulsion being filtered through a layer of the esters.

Sinha and Ganguli[7] have drawn attention to the fact that certain emulsions are broken by the action of ultra-violet light. For breaking

[1] Ill. State Geol. Survey, *Rept. Investigations*, No. **29**, 7—38 (1933).

[2] *Petroleum World*, **29** (iv), 47 (1932).

[3] *Petroleum Engr.*, **2** (iii), 57, 60 (1930).

[4] *Natl. Petroleum News*, **20** (42), 119, 124 (1928).

[5] U.S. 1,987,870 (1935).

[6] Fr. 706,809 (1930).

[7] *Kolloid-Z.*, **54**, 147 (1931).

crude oil emulsions, Herbsman[1] claims irradiation with ultra-violet light, X-rays, cathode rays, canal rays or rays from radio-active substances.

According to Beckman,[2] natural crude-oil emulsions containing an emulsifying agent are treated with a medium adapted to sustain the life of, and are inoculated with, living micro-organisms which are capable of destroying such emulsifying agent. The emulsion is agitated and maintained at 20°—40° C.

Finally, attention is drawn to an important report by Lane *et al.*[3] on typical methods and devices for handling oil-contaminated water from ships and industrial plants. A study of the breaking of emulsions has been made by Edgerton and Germeshausen,[4] using the stroboscope and high-speed motion-picture camera.

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[1] U.S. 1,783,471 (1930); Brit. 356,926 (1930): Ger. 592,877 (1934).

[2] U.S. 1,753,641 (1930).

[3] U.S. Bur. Mines, *Tech. Paper*, **385**, 1—60 (1926).

[4] *Am. Inst. Chem. Eng.*, New York Meeting, May 14/16, **1934**, 17 pp.

APPENDIX II

Summary of important patents since 1934.

CHEMICAL METHODS

(1) De Groote and associates (U.S. Patents).

(1934)	1,954,585 1,976,602 1,977,048 1,984,633
(1935)	1,988,832/3/4/5 1,994,758 2,015,260 2,023,993/4/5/6/7 2,025,803/4/5 2,026,217/8/9
(1936)	2,037,885/6 2,050,923/4/5/6/7 2,052,281/2/3/4
(1937)	2,076,623/4 2,077,229/30 2,077,745/6 2,079,762/3/4 2,081,003/4/5 2,083,220/1/2/3/4/5 2,085,298/9 2,086,215/6/7
(1938)	2,104,793/4/5
(1939)	2,166,431/2/3/4 2,167,346/7/8/9 2,176,702/3/4
(1940)	2,153,744/5/6 2,154,422/3 2,192,993/4 2,194,643/4/5/6 2,216,312
(1941)	2,231,752/3/4/5/6/7/8/9

(2) Various authors. (U.S. Patents.)

Blair	2,159,312 (1939) 2,216,310 (1940)
Burwell	1,993,646 (1935)
Colbeth	2,058,568 (1937) 2,114,651 (1938) 2,122,976 (1938) 2,183,487 (1939)
Cushman	2,191,372 (1940)
Hendry and Ebaugh	2,014,936 (1935)
Herbsman	2,087,936 (1937)
Hershman	2,153,560 (1939)
Lerch	1,890,789 (1932) 1,990,293 (1935)
Mering	2,209,445 (1940)
Oberlin	2,089,035 (1937)
Powell	2,175,699 (1940)
Roberts	1,977,089 (1934) 1,985,692 (1934) 2,000,717 (1935) 2,023,976 (1935)
Shapiro	2,217,387 (1940)
Staten	2,191,357 (1940)
Stehr	2,023,979/80/1/2 (1935) 2,026,195 (1935)
Stryker	2,175,818 (1940)
Suthard	2,206,062 (1940)
Talley and Gutzeit	2,167,327 (1939)
Vogt and Smeykal	2,216,257 (1940)
Walker	2,000,725 (1935)
Wayne	2,214,783/4 (1940)

GRAVITY METHODS

Bailey	1,983,832 (1934)
Hawley	2,214,248 (1940)
Stewart	2,188,018 (1940)

THERMAL METHODS

Curtin	1,973,430 (1934)
Hays	2,082,337 (1937)
Millard	2,179,131 (1939)
Woelflin	2,047,538 (1936)

ELECTRICAL METHODS

Adams and Barlow	2,092,491 (1937)
Dillon	2,038,479 (1936)
Eddy	2,033,129 (1936) 2,033,446 (1936) 2,083,801 (1937) 2,216,724 (1940)
Fisher	2,033,143 (1936)
Hanson and Eddy	2,033,429 (1936)
Heinrich	2,000,018 (1935)
Hill	2,033,593 (1936)
Mahone	2,216,977 (1940)
McDonald	2,033,418/19/20 (1936)
Passler and Brunnbauer	Brit. 481,121 (1938)
Pettefer	2,033,567 (1936)
Prutzman	2,027,615/16 (1936)
Roberts	2,033,152 (1936) 2,083,798/9 (1937)
Sauer	2,136,469 (1938)
Woelflin	2,083,800 (1937) 2,083,802 (1937)
Wolfe	2,096,774 (1937)
Worthington	2,001,809 (1935) 2,033,167 (1936) 2,034,285 (1936)

See also :

Slonim and Beklemishev	**Russian 47,387** *Chem. Abs.*, **33**, **2687 (1939)**
Siemens-Schuckertwerke A.-G.	**Ger. 647,999 (1937)**
Passler	***Bohrtech.-Ztg.***, **55**, **59 (1937)**

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